PB86-121365

In-Situ Methods to Control Emissions from Surface Impoundments and Landfills

Arkansas Univ., Fayetteville

Prepared for

Environmental Protection Agency, Cincinnati, OH

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS.

PB86-121365

EPA/600/2-85/124
October 1985

IN-SITU METHODS TO CONTROL EMISSIONS FROM SURFACE IMPOUNDMENTS AND LANDFILLS

by

Charles Springer
Kalliat T. Valsaraj

Department of Chemical Engineering
University of Arkansas
Fayetteville, AR 72701

Louis J. Thibodeaux
Louisiana State University
Baton Rouge, LA 70803-6421

CR 810856-01-1

Project Officer

Paul R. de Percin
Land Pollution Control Division
Hazardous Waste Engineering Research Laboratory

Hazardous Waste Engineering Research Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Cincinnati, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/2-85/124		PB86 121365/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
In-Situ Methods to Control Emissions from Surface Impoundments and Landfills	October 1985
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Charles Springer, K. T. Valsaraj Louis J. Thibodeaux	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
University of Arkansas Fayetteville, Arkansas 72701 Louisiana State University Baton Rouge, LA 70803	BRD1A 11. CONTRACT/GRANT NO. CR-810856

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Hazardous Waste Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Final Report 10/83 - 9/85 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Paul R. dePercin, Project Officer (513) 569-7797

16. ABSTRACT

This report presents the results of a two-year study which included laboratory investigations as well as comprehensive literature review on methods of reducing the rate of emissions of volatile chemicals from surface impoundments and landfills.

The report presents information on the following in-situ methods which may be employed to reduce emission rates:

- Air supported structures
- Floating solid objects
- Shape modification
- Aerodynamic modification
- Floating oil and/or surfactant covers
- Synthetic membranes over landfills.

Conclusions are drawn with respect to the suitability of each of the methods under various circumstances and the degree of control which might be expected.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	83
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $11.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement number 810856-01-1 to the University of Arkansas. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes methods which may be used to reduce the rate of volatile chemical emissions from surface impoundments and landfills, and will be useful to treatment, storage and disposal facilities operators and designers as well as regulatory personnel. For further information, please contact the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Enginering Research Laboratory

ABSTRACT

This report presents the results of a two-year study which included laboratory investigations as well as a comprehensive literature review on methods of reducing the rate of emissions of volatile chemicals from surface impoundments and landfills.

The report presents information on the following in-situ methods which may be employed to reduce emission rates:

- Air supported structures
- Floating solid objects
- Shape modification
- Aerodynamic modification
- Floating oil and/or surfactant covers
- Synthetic membranes over landfills

Conclusions are drawn with respect to the suitability of each of the methods under various circumstances and the degree of control which might be expected.

This report was submitted in fulfillment of Cooperative Agreement No. 810856-01-1 by the University of Arkansas under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from Octiber 1, 1983 to September 30, 1985.

TABLE OF CONTENTS

Section		Page
1.0	INTRODUCTION	1
	1.1 Scope	1
	1.2 General Considerations in the Choice of a Control Technique	1
	1.3 Oxygen Reaeration	2
2.0	GENERAL CONCLUSIONS	3
	2.1 Complete Enclosure of a Surface Impoundment	3
	2.2 Floating Solid Objects	3
	2.3 Shape Modification of Surface Impoundments	4
	2.4 Aerodynamic Modification	4
	2.5 Floating Oil Layers and Surfactants	4
	2.6 Synthetic Liner Covers for Landfills	5
3.0	COMPLETE ENCLOSURE OF SURFACE IMPOUNDMENTS BY AIR SUPPORTED STRUCTURES	6
4.0	FLOATING SOLID OBJECTS	7
	4.1 Floating Synthetic Liners	7
	4.2 Rafts	7
	4.3 Floating Hollow Spheres	8
5.0	SHAPE MODIFICATION	9
	5.1 Berm Height	9
	5.2 Impoundment Depth	10
	5.3 Orientation of an Impoundment and Length to Width Considerations	10
6.0	AERODYNAMIC MODIFICATIONS	12
	6.1 Conclusions	25
7.0	FLOATING OIL COVERS AND SURFACTANTS	27
	7.1 Oil Cover--No Wind Conditions	28
	7.2 Oil Cover--Windy Conditions	43
	7.3 Use of Surfactants as a Control Option	55
	7.3-A No-Wind, Stagnant Conditions	55
	7.3-B No-Wind, Stirred Conditioon	57
	7.3-C No-Wind Condition, Warm Water-Cold Air Scenario	61
	7.3-D Wind-enhanced Conditions	61
8.0	SYNTHETIC MEMBRANES OVER LANDFILLS	63
9.0	LITERATURE CITED	70

LIST OF FIGURES

Figure No.	Title	Page
6-1	Wind Tunnel/Water Tank Simulator	14
6-2	Sampling Tube Arrangement	15
6-3	Fence Arrangements on Water Surface	18
6-4	Liquid Phase Mass Transfer Coefficient vs. Fence Height	19
6-5	Liquid Phase Mass Transfer Coefficient vs. (F/h)	20
6-6	VOC Control vs. Fence Height	21
6-7	Log-Plot of Liquid Phase Coefficient vs. (F/h)	22
7-1	Interfaces in the Control Septem	29
7-2	Simulator for Surface Impoundment Under No-Wind Conditions	31
7-3	Experimental Results for Benzene Under Different Mineral Oil Thicknesses	34
7-4	Experimental Results for Acetone Under Different Mineral Oil Thicknesses	35
7-5	Experimental Results for n-propanol Under Different Mineral Oil Thicknesses	36
7-6(a)	Experimental Results for Acetone Under Octanol Cover (Surface Partially Covered)	38
7-6(b)	Experimental Results for Acetone Under Octanol Cover (Surface Fully Covered)	39
7-7(a)	Experimental Results for Acetone Under Lauryl Alcohol Cover (Surface Partially Covered)	40
7-7(b)	Experimental Results for Acetone Under Lauryl Alcohol (Surface Fully Covered)	41

7-8	Fractional Emission Reduction vs. Cover Thickness	43
7-9	Oil Layer on an Impoundment Surface Under Influence of Wind	46
7-10	Wind-Tunnel Arrangement	47
7-11	Wedge-Shape Oil Slick Model	53
7-12	Phase Resistances in a Surfactant System	57
7-13	Bulk Eddy Disturbance in Surfactant Solutions	60
8-1	Landfill Cover Scheme Using Synthetic Membrane	65

LIST OF TABLES

Table No.	Title	Page
6-1	Scaling Factors for Laboratory Simulators	16
6-2	Fence Control Simulation Results	24
7-1	Chemical Properties of Experimental VOC	33
7-2	Fractional Reduction in Emissions Using Various Mineral Oil Layer Thicknesses	33
7-3	Emission Reduction for Acetone Using Octyl Alcohol and Lauryl Alcohol as Immiscible Covers	37
7-4	Results of Wind-Tunnel Tests on a Partial Coverage of Oil Layer	51
7-5	Results of Oil Slick Observation Experiments	54
8-1	Diffusivities of Several Chemical Vapors in a 20-Mil Sample of Poly(vinylchloride) Film	68
8-2	Apparent Diffusivities of Chemical Vapors in a 20-Mil Sample of Poly(vinylchloride) Film	70

1.0 INTRODUCTION

1.1 Scope

This document finalizes a study conducted under the sponsorship of the United States Environmental Protection Agency (EPA) to evaluate in-situ control methods which might be readily adopted for use at existing treatment, storage and disposal facilities (TSDF) for the purpose of reducing emissions of Volatile Organic Chemicals (VOC). Emissions of VOC from TSDF's are a significant source of contaminants entering the atmosphere. Bretton, et al. (1983) reported that at least one-third of the total emissions of over 50 volatile, hazardous chemicals are from TSDF's. These chemicals are the most volatile and toxic chemicals regulated under the Resource Conservation and Recovery Act (RCRA).

The main focus of federal and state regulations of TSDF's in the past has been to minimize contamination of surface and ground water, to prevent air contamination from incineration and to prevent accidental exposure. However, more recently, attention has been directed to the problem of emissions from TSDF's.

A considerable amount of work has been done in quantifying impoundment and landfill emissions (Springer, Thibodeaux, et al., 1983, 1984 and Lunney et al., 1984). Simplified models of the mass-transfer processes were developed and shown to be generally valid. With that background, it was possible to propose methods to reduce the emissions. Some control methods simply interpose a physical barrier between the impoundment and the atmosphere, while others attempt to modify the mass transfer process in more subtle ways to bring about reductions.

This work was undertaken to examine controls which might be added to existing facilities in order to reduce direct emissions from surface impoundments and landfills.

The methods treated in this document include:

Complete, positive control by use of an enclosure which precludes loss of any vapor to the air, such as a domed structure of synthetic membrane covering the entire impoundment.

Floating solid objects which restrict the exposed surface area of the impoundment.

Modification of the shape of the impoundment.

Aerodynamic modifications.

The addition of other materials, such as oils or surfactants to the impoundment.

The use of synthetic liner type membranes over landfills.

1.2 General Considerations in the Choice of a Control Technique.

To evaluate a control scheme and to make a choice of control method, one must take into consideration the purpose of the impoundment and the goals of the

control strategy. Frequently the reduction or elimination of emissions may only delay the process until some other time. To entirely prevent volatile emissions there must be some method of destruction of VOC, which presumes some method of capture after removal from water.

If the goal is to reduce the rate of emission, thus, to reduce the concentration of VOC at some receptor location, then an absolute elimination might not be necessary.

The parameters affecting the emission rate include the wind as well as the size and orientation of the surface impoundment. The mass transfer process which governs the volatilization of almost all the chemicals of interest is the liquid phase process. Since this is so, then differing rates from one chemical to another are largely a matter of liquid phase diffusivity differences, and the rates do not vary from one chemical to another, in the usual case, due to vapor pressure variations. The assumption in this instance is simply that the volatility is high enough so that it is not generally limiting. The temperature of the water has a marked effect upon the diffusivity, the diffusivity increases approximately as the 1.8 power of the absolute temperature. Thus, a higher liquid temperature favors more rapid volatilization.

Control techniques which tend to change the gas phase resistance will be effective for only a few chemicals, those with very low Henry's law constants. Such materials will display low vapor pressure and/or higher solubility in water.

When immiscible, volatile materials float on the surface, the emission rate will be greatly influenced by the gas phase resistance which is normally quite low compared to the liquid phase resistance. Such instances will be characterized by extremely rapid volatilization.

1.3 Oxygen Reaeration

If an impoundment is being used to carry out aerobic digestion, then a continual resupply of oxygen is necessary.

The transfer rate of oxygen from the air to the water is governed entirely by the liquid phase mass transfer process. Thus, any device or technique which restricts volatilization by reducing the mass transfer coefficient in the liquid phase will necessarily reduce the oxygen transfer rate accordingly.

Similarly, devices such as aerators which are ostensibly intended to increase the oxygen transfer will simultaneously increase the volatilization rate accordingly.

If an aerobic digestion is desirable in a surface impoundment, some of the emission control techniques will be inappropriate.

2.0 GENERAL CONCLUSIONS

There are a number of options available which would serve to reduce the rate of emissions from surface impoundments. Choosing among the options will involve consideration of the goals and circumstances surrounding the application.

Specific conclusions relating to the various options considered and/or studied in this work are given below:

2.1 Complete Enclosure of a Surface Impoundment.

Complete enclosure of a surface impoundment by an air-supported structure is a feasible control method if the vapors are collected and disposed of. This method is perhaps the only control technique which would be feasible if a surface aerator were to be used to improve oxygen transfer. Air supported structures are susceptible to wind damage as well as weathering. Some vapors may be harmful to the polymeric materials. The control effectiveness can approach 100%

2.2 Floating Solid Objects

Floating solid objects include synthetic membrane covers, rafts, and hollow plastic spheres.

Floating synthetic membrane covers have been successfully used and will be feasible if oxygen transfer is unnecessary and if outgassing of volatiles is not expected. Some liner material may be highly permeable to some organic vapors. The floating membrane will be subjected to damage by weathering or by contact with the waste. The control effectiveness can approach 100%.

Rafts, and other such structures will restrict the surface area of an impoundment exposed to the air and will reduce emissions accordingly. Rafts will also cause reduced oxygen absorption; many will have a short lifetime due to damage by contact with the wastewater. The maximum control effectiveness of rafts will be about 90%.

Floating hollow spheres have been shown to reduce emissions by as much as 80 to 90%. The most popular type of sphere is made from polypropylene and has projections to prevent rotation in the wind. The spheres will restrict oxygen absorption to the same degree that they reduce emissions; however they may be blown away in a high wind.

2.3 Shape Modification of Surface Impoundments

Shape modification is meant to include berm height, liquid depth, length or width of the impoundment and directional orientation.

Increasing berm height is an effective method of emission reduction although the effectiveness cannot be accurately predicted. This method will be effective in reducing wind-enhanced emissions

For a given impoundment volume, increasing impoundment water depth will cause emission reduction by reducing the ratio of surface area to volume. Wind-enhanced mass transfer coefficients may also be reduced if the actual water depth were increased.

Wind-enhanced emissions can be reduced if the fetch (down-wind distance) is reduced. Relatively narrow impoundments will have lower emissions if the wind is blowing normal to the longer dimension of the impoundment.

2.4 Aerodynamic Modification

Laboratory investigations of the effectiveness of wind barriers shows them to be quite effective in reducing emissions under wind-enhanced conditions. The performance of perimeter fences and of network fences were found to be generally similar. The mass-transfer coefficient was found to be approximately proportional to the square root of the fetch to height ratio, up to a maximum of 160. A commercial, porous wind fence material commonly used for dust control was found to be much superior to solid fences. Wind fences can potentially achieve emission reduction of up to 80%. Oxygen absorption will be effected similarly.

2.5 Floating Oil Layers and Surfactants

A layer of immiscible liquid floating on the surface of an impoundment was found to be quite effective in reducing emissions. Under conditions of little wind it was observed that volatile materials with low solubility in the oil cover material were controlled more effectively than those which are more soluble. However, an oil covering of about one cm depth would provide at least 90% emission reduction for any volatile.

In the presence of a wind, the covering may be blown aside. Under windy conditions, the effect of solubility is variable. With low winds, a low solubility in the oil is preferable, but with higher winds a high solubility is preferable. The mixing action of higher winds tends to cause the volatile solute to transfer to the oil phase where emission mass transfer coefficients are markedly lower. For the windy conditions, emission reduction is better than a simple ratio of exposed to covered area would predict. Emission reduction of 50 to 80% may be expected for windy conditions, depending upon the amount of oil used.

Oxygen absorption will be reduced in accordance with the fraction of the surface which remains covered by the oil layer.

The action of surfactants has not been adequately studied. The adding of surfactants to the water of a surface impoundment is believed to result in a significant emission reduction, but additional research would be required to quantify the effect.

2.6 Synthetic Liner Covers for Landfills

Laboratory measurements of the vapor phase permeability of a 20-mil poly (vinylchloride) membrane showed a high permeability for a number of volatile organics. Little data on the permeability of various polymers to vapors is available.

The performance of a membrane as a vapor barrier cannot generally be predicted and may be disappointing.

Simple laboratory tests are available to measure the permeability of specific membrane materials to specific vapors.

3.0 COMPLETE ENCLOSURE OF SURFACE IMPOUNDMENTS BY AIR SUPPORTED STRUCTURES

Snythetic covers have been proposed for use as totally enclosing covers (direct control). If a liner is placed over the impoundment and sealed around the periphery, a system of hermetic integrity can be created. The covering is then held rigidly in place by inflation. Such installations are termed "air supported structures". Vapors which rise from the impoundments may be bled off and disposed of in an appropriate manner, e.g., incineration or carbon adsorption. An installation of this nature would be similar in effectiveness and function to that of a covered, vented tank. Vogel (1985) discusses the costs of fume incinerators for vented tanks.

A test performed by Radian Corporation, (Wetherold, 1985) indicated that direct control was ineffective when a carbon adsorption system was employed to trap organic emissions from the purge air stream. Material balances indicated that most of the volatile hydrocarbons passed through the adsorption bed because of the high moisture content of the air stream. The conclusion was that the control method tested was ineffective because of adsorption site competition from the water vapor. An alternative method for removal of vapors from the vent gas might make this direct control a viable method.

The properties of the covering material will affect the service life of an air supported structure. The important properties are resistance to weathering, including especially ultra-violet radiation and compatibility with the organic material being contained. Haxo (1980) presents chemical compatibility data for a number of synthetic materials, along with weather and tear resistance ratings. Some of the membrane materials tend to crack in cold weather and all are subject to damage by high winds.

Permeation through the cover may be significant for some combinations of synthetic liner and VOC. An extensive data base of liner permeability to vapors is not readily available. Fortunately, however, a relatively simple laboratory test, similar to the ASTM test for water vapor permeability, can be used to obtain specific permeability data. The test consists of placing a liquid sample of the VOC in a small container (glass jar) and sealing a piece of the synthetic liner over the opening with a ring made by cutting a hole in a screw-cap. The container is then weighed at appropriate time intervals and the rate of weight loss is noted over time. Such a test would normally require only a few weeks at most. Thus, lack of a data base need not prevent the use of this control technique.

An important advantage of the air supported structure is that any appropriate re-aeration scheme can be used without an attendant increase in emission (providing that the vent trapping effectively eliminates release of VOC). This would be advantageous if aerobic digestion were desirable.

4.0 FLOATING SOLID OBJECTS

There are a variety of control methods employing floating objects, all of which function by reducing the exposed area. The effectiveness of floating objects will be essentially a linear function of the fraction of the area covered. That is, a device which covers 50% of the impoundment would reduce the emission rate by about 50%.

4.1 Floating Synthetic Liner Covers

Synthetic liners have been used as floating covers on potable water reservoirs since the early 1970's (Evans and Meade, 1984). The covers are also being employed at certain superfund sites to restrict the inflow of rain water. There have been at best two such covers, with apropriate installation methods patented (U.S. Patent 3,980,199, 1976 and U. S. Patent 3,991,900, 1976). Cudahy and Standifer (1980) reported a number of applications of floating, gas-tight covers over surface impoundments as odor control strategies.

The chemical compatibility concerns are similar to those of the air supported structures except that covers actually in contact with the impoundment liquid may suffer degradation from non-volatile solutes as well as volatile solutes. Where there are gases generated and/or liberated, a method must be provided for the collection. One of the patents mentioned provides for gas collection. Disposal or destruction of the hazardous constitutents in the gas must be treated similarly to that from the air supported structures. Again, high relative humidity would interfere with adsorption as a collecting agent.

Evans and Meade (1984) reported some extreme weather conditions, including ice accumulation and very low temperatures (-65°F) as well as very high winds at another installation (150 mph) which did not cause failure of the covers.

The floating cover will provide essentially 100% containment of volatile emissions if a satisfactory adsorption or incineration method is used to clear the vent gases. Biological processes which might occur can generate gases which must be vented. Permeation is a potential problem, perhaps somewhat more so than with air supported structures. The floating cover is not suited to the control of emissions from aerobic digestion processes.

4.2 Rafts

Rafts floating on impoundment surfaces are not widely used. However, the effectiveness of a raft in emission reduction will be a function of the fraction of the surface covered. Ehrenfeld and Ong (1985) suggest that the upper limit of the surface coverage is about 90%, which would reduce emissions accordingly. An exception would be for emissions from impoundments where some immiscible volatile material less dense than water is present in excess of its solubility (floating volatile). In such a case, one would expect the organic phase to seek out the exposed surface from under the raft. The raft would thus be ineffective in such a case.

As with other covers, problems of chemical compatibility must be considered. Rafts constructed of wood can be expected to have a relatively short life unless built of resistant species or elaborately protected. Treated lumber may cause hazardous material to be leached out, adding somewhat to the hazardous waste burden.

The use of rafts will restrict oxygen transfer to the water in about the same proportion as they will reduce emissions.

4.3 Floating Hollow Spheres

Floating hollow spheres, similar to table tennis balls were first used as an evaporation control on reservoirs. However, wind induced rotation of the balls, resulting in continual exposure of a thin film of liquid to the air actually enhanced the evaporation process. Shortly, polypropylene spheres with rotation-inhibiting projections were made available. Cudahy and Standifer (1980) reported on the use of such spheres to reduce odors. Vogel (1985) reports that hollow polypropylene spheres (with rotation inhibiting projections) are commercially available in several diameters ranging from 20 mm to 150 mm, and that emission control effeciencies of up to 90% can be achieved while simultaneously heat exchange with the atmosphere is reduced by 75%. Ehrenfeld and Ong (1985) point out that the theoretical maximum area reduction with a simple layer of spheres is approximately 91%.

Very small spheres have been used to retard emissions from crude-oil storage tanks (Cudahy and Standfer, (1980). This application used a blanket of up to 2.5 cm thick. Evaporation losses were reduced by 50 to 70% for working tanks and 70 to 90% for static tanks.

An important limitation on the use of floating plastic spheres for outdoor surface impoundments would be the tendency for these to be blown away in a high wind. Certainly, one would expect that the very small spheres could be easily blown away.

The spheres would be expected to reduce oxygen uptake to the same extent that emissions were reduced. Thus, one would not employ the floating spheres to control emissions if aerobic digestion were desired.

5.0 SHAPE MODIFICATION

Although it may be only infrequently possible or feasible to change the shape or orientation of a surface impoundment, there are a number of ways in which improvements in emission control can be achieved, simply by changes in the impoundment design. Included among the shape modification considerations are: berm height, impoundment depth and length to width and directional orientation.

5.1 Berm Height

Perhaps the easiest and simplest shape modification, and maybe the only shape modification that could be considered as a truly in-situ technique would be modification of the berm height.

There has been little, if any, actual studies of the effect of berm height on wind-enhanced emissions. Our work on aerodynamic modification (described in Section 6.0) is probably the most nearly related experimental work available. Levich (1962) presents theoretical considerations involving mass-transfer in the valleys between projections upon a rough surface. Levich suggests an inverse proportionality between the square root of the projection height and the mass transfer coefficient, i.e $k \propto (1/h)^{0.5}$, where k is the mass transfer coefficient and h is the projection height.

There are two important limitations to the immediate application of this relationship to emission reduction at a surface impoundment.

The first limitation is that the simple relationship does not take into account the effect of distance between projections, or in terms of a surface impoundment, the fetch. Rather, the expression is predicated upon the fetch being no more than three to five times the projection height.

The affected region of an impoundment downwind of the berm will be that region upwind of the point where the velocity profile is re-established. Thibodeaux, et. al. (1981) suggests this distance as being about 20 projection heights. Our work with aerodynamic modification concludes that fence-type projections will have no utility beyond 160 projection heights. However, this is considering an average influence over the entire surface. The presumption is that the net effect will be negligible if the fetch is beyond 160 projection heights.

The second limitation to the application of Levich's approximation is that it applies to a gas phase coefficient, while normally, the surface impoundment emission rate is a function of the liquid phase coefficient. However, there is a very large body of information to suggest that liquid phase behavior is strongly influenced by adjacent gas phase turbulence and flow patterns, and although we are unable to quantify the effects in some specific cases, such as the present instance, we know that there will be a significant influence.

We can safely conclude that increases in berm height and/or lowering of liquid level in an impoundment will cause a marked reduction in wind-enhanced emission rates. It should be anticipated that reduction of up to 50% may be achieved in this manner, depending upon local circumstances.

5.2 Impoundment Depth

The depth of an impoundment will have a profound effect upon the volatilization rate of VOC. While there are cogent reasons for limiting the impoundment depth in order to minimize the extent and/or likelihood of ground water contamination, it is never-the-less possible to exercise a considerable control over the emission rate by an increased liquid depth.

For a given volume of liquid, it is obvious that the exposed surface area will be inversely proportional to the depth, which as a first approximation, can be directly related to the emission rate since that rate is approximately proportional to the area. However, Lunney (1983) points out that wind-induced turbulence of the liquid layer is greater for shallower liquid layers, thus an increased depth does, by itself, reduce the mass transfer coefficient. The effect is difficult to quantify, but Lunney (1983) and Lunney, et. al (1984) show the effect of depth empirically in terms of the ratio of fetch (the distance across the impoundment in the wind direction) to depth ratio (F/D). A typical surface impoundment will have a fetch to depth ratio of 75 or more. However, as this ratio is reduced below about 50 (depending upon wind velocity) the mass transfer coefficient will decrease as well. Thus, it may be reasonably anticipated that increased depth will bring about a decreased mass transfer coefficient, quite apart from any accompanying reduced area effect. Lunney also pointed out that at some further depth, known generally as the "Ekman depth" the surface induced flows no longer prevail. Solutes residing in liquids (or as immiscible, heavy chemicals lying on the bottom) would be transferred only by the relatively slow process of molecular diffusion. Thus, mass transfer in such a case would not be a function of any surface activity but rather would be limited by the slow transfer rate below the Ekman depth. Lunney, et al. (1984) show evidence that the Eckman depth may be of the order of one-tenth the fetch.

It is somewhat unlikely, however, that the depth of any impoundment would ever exceed the Ekman depth.

An increased impoundment depth, for a given volume, will decrease emissions in a non-linear fashion. The rate of oxygen uptake would be reduced accordingly.

5.3 Orientation of an Impoundment and Length to Width Considerations

While it is probably only rarely possible to alter the shape orientation of a surface impoundment, it may be well to consider some of the subtle effects that might be achieved in locating and sizing with respect to prevailing wind direction.

For a relatively shallow impoundment, where the entire depth is within the turbulent zone, Lunney, et al. (1984) showed that the ratio of fetch to depth exhibited an influence on the wind-enhanced emission rate. These results showed a constant, or declining mass transfer coefficient as the fetch to depth ratio (F/D) was increased to about 14, but as the ratio was increased further, the mass transfer rate increased to generally, about 50% greater than the minimum, until, at a ratio of about 50 (F/D) the mass transfer ceased to vary with the ratio.

Taking the foregoing into account, and also allowing for the effect of berm height considered earlier, it would be appropriate to so locate and situate an

impoundment so that it is relatively narrow in the prevailing wind direction, that is, with the longer dimension at right angles to the wind. If, besides maintaining a low fetch to depth ratio, one were to also keep the narrow fetch below about twenty times the berm height, emission reductions of at least 50% or perhaps as much as 75% could be achieved relative to less favorable orientations. Alternately, if sensitive receptors (homes, etc.) were located at one direction away from the impoundment site, advantage might be taken of favorable orientation by maintaining a narrow fetch in the direction of those receptors. Thus, whenever the wind were blowing in the direction of nearby homes, a lower emission rate would be achieved at such times. In addition, the impoundment would then be closely approximated as a line source of emission with a resulting lower value for maximum downwind concentration.

6.0 AERODYNAMIC MODIFICATIONS

Volatilization is an important pathway for emission of volatile organic chemicals (VOCs) from surface impoundments. The general mechanisms of this process have been explored in detail by Thibodeaux (1979). Here we give a brief review of these mechanisms with particular emphasis on the mass transfer concepts of relevance here.

Consider a situation where a chemical (VOC) of concentration $C_W(kg/m^3)$ is present in the aqueous phase of a surface impoundment with an overlying air which contains a concentration $C_A(kg/m^3)$ of the same chemical. The concentrations C_A and C_W are related through a Henry's constant, H. If C_A/H is less than C_W, then we say that volatilization of the compound is said to occur. The overall rate of volatilization is a first order process given by

$$N = K\,(C_W - C_A/H) \qquad (6\text{-}1)$$

where N is the emission flux of chemical A from the water surface, $kg/m^2.s$
K is the overall mass transfer coefficient, m/s.
H is the Henry's constant for the volatile species in m^3 water per m^3 air.

The overall mass transfer coefficient K can be expressed as a combination of individual phase mass transfer coefficients

$$\frac{1}{K} = \frac{1}{k_\ell} + \frac{1}{k_g H} \qquad (6\text{-}2)$$

Each term on the right hand side of equation (6-2) represent a resistance. The first term $1/k_\ell$ represents the liquid phase resistance while the second term $1/k_gH$ represents the gas phase resistance. The coefficients k_ℓ and k_g are both functions of several important variables like wind velocity, temperature etc. Each of these terms must account for both mechanically and naturally stimulated processes. Wind is a natural process which influences the volatilization process in a surface impoundment. It effects both k_ℓ and k_g; k_ℓ is proportional to square of the wind velocity while k_g varies proportionally to the wind velocity. In the absence of wind, the temperature difference between air and water is the controlling factor, i.e., both k_ℓ and k_g are proportional to $T^{1/4}$. Mechanical surface aerators placed in surface impoundments also have a dramatic effect on k_ℓ and to a lesser extent on k_g.

Inspection of equation (6-1) indicates that the overall emission flux, N can be reduced in two ways, either by reducing the concentration of the VOC in water or by reducing K. The effect of wind fences (both perimeter and network) to interrupt the wind over a S.I. involves reducing K.

Parker (1984) developed an expression relating k_ℓ to the protrusion height (height of a wind fence above the impoundment) using concepts developed earlier by Levich (1962[b]) and using the Chilton-Colburn analogy. This expression is given below

$$k_\ell = (\text{constant})\, h^{-1/2} \qquad (6\text{-}3)$$

where h is the vertical height. This expression indicates that as the height of the wind fence increases the value of k_ℓ decreases as square root of h.

We conducted a series of experiments to test this prediction using solid network, solid perimeter and porous perimeter fences tilted at various angles towards the wind.

Volatile organic chemical emissions from a lagoon were simulated in a wind tunnel/water tank simulator modeled after Mackay (1978). The wind tunnel section was 16 ft (4.9m) long with approximately a square conduit 2 ft (0.6m) by 2 ft. The water tank was 8 ft (2.4m) long, 2 ft (0.6m) wide and had a false bottom such that tank depth could be changed. Figure 6-1 is a schematic drawing showing the wind tunnel arrangement.

The wind tunnel/water tank simulator was constructed of epoxy coated plywood and plexiglass. The test section was accessed through two 0.5m by 0.4m rectangular doors.

The water tank test section depth was 5.457 cm, an average of fourteen measured depths. The water tank test section had a fetch to depth ratio (F/D) of 44.7. Sampling tubes were arranged within the tank section as shown in Figure 6-2. Teflon tubing (2 mm) was supported by sheetmetal ells to a sample intake height of approximately 2.7 cm from the tank bottom. The ells and tubing runs were attached to the bottom and side of tank with silicone rubber caulk. All sample tubing exited on the right side of test section.

A one horsepower motor powered the blower to pull air through the wind tunnel. Air flow through the tunnel was controlled by inserting flow restricting baffles preceding the blower intake. Wind velocities were measured with a Kurz Model 444 air velocity meter. With the baffle in place a velocity at 10 cm height (V(10 cm)) of about 2.9 m/s was measured while no flow restriction resulted in V(10 cm) of about 3.9 m/s. These velocities correspond to velocities in the field at 10 m height (V(10m)) of 5.6 cm/s and 8.0 m/s by applying the 1/7th power law. Reproduction of Renolds' number is not required. Provision of turbulent boundary layers assured that prototype flow patterns were duplicated if correct scaling was used (Snyder, 1972).

The wind/water tank test section was equipped with a liquid level controller as described by Lunney (1983). The water reservoir cylinder in this case was smaller and replacement water flow was by gravity. The reservoir cylinder change in volume per change in measured height was 51.01 ml/cm.

The fences were constructed of sheet metal with nylon Velcro (TM) attached to the sides. The hook side of the Velcro (TM) was situated on the wind tunnel walls to result in the desired placement of the fence. A bead of silicone rubber caulk was placed along the bottom of the fence to prevent flow under the fence. Commercial wind fence material, DustTamer (TM) model 65-10, was cut to simulate a 4.8 m prototype fence. Silicone rubber caulk was heavily applied to the sides and one long edge of the model fence. The fence was then stretched taut with spring tension rods at the leading edges of the test section. When the caulk had dried the rods were removed. This attachment closely resembles field installation of the DustTamer.

Fence dimensions were determined from a fence height (h) to lagoon fetch (F) ratio:

$$h(L)/F(L) = h(m)/F(m).$$

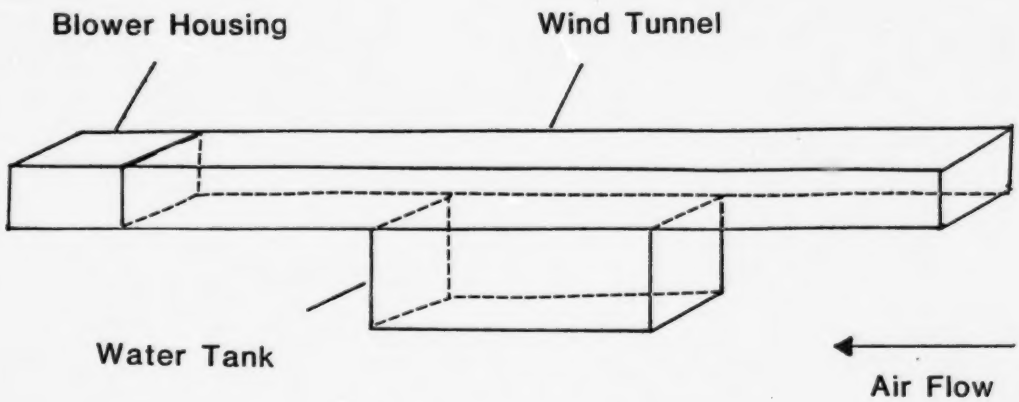


Figure 6-1: Wind Tunnel/Water Tank Simulator

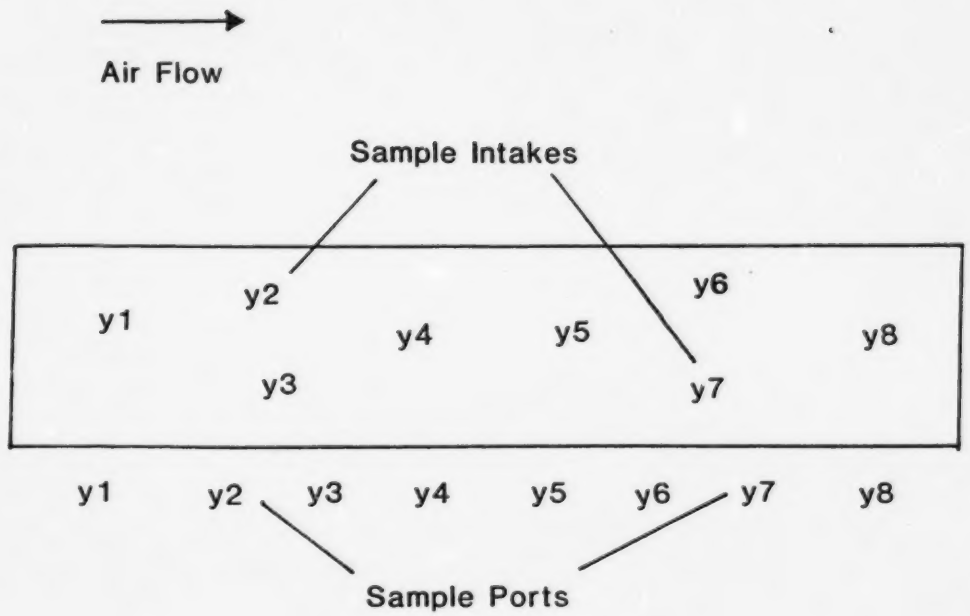


Figure 6-2: Sampling Tube Arrangement in Water Tank

The L refers to measurement of actual lagoons and m refers to the measurements of the water tank. A 2.4 m (8 ft) fence height was assumed for the lagoon based on snow fence studies. Lagoon fetch (186 m) was scaled from field measurements of an existing surface impoundment studied at one particular hazardous waste facility in Western New York state. This surface impoundment was nearly square in plan area with sides of 186 meters and 4.23 meters in depth. Table 6-1 shows the relation and scaling factors between the field impoundment and the laboratory model.

Table 6.1 Scaling Factors for Laboratory Simulation

Parameter	Laboratory Model	Field Equivalent
Wind Speed	2.90 m/s at 10 cm	5.6 m/s at 10m
Wind Speed	3.90 m/s at 10 cm	8.0 m/s at 10m
Fetch*/depth ratio	44	44
Fetch*	2.44 m	186 m
Fence height	3.2 cm	2.4 m
Fence height	1.7 cm	1.2 m
Fence height	6.4 cm	4.8 m

* Fetch = distance wind travels over open water. In this study it is the distance between fences, or fence spacing.

Ethyl ether was chosen as the test chemical as it is considered to be 100% liquid phase controlled (Lunney, 1983). It is used in health applications and is not considered carcinogenic or teratogenic.

Gas chromatography was used to detect loss of chemical from the liquid in the tank section. Tracor 565 and Perkin Elmer Sigma 3B gas chromotograph were fitted with 8' s.s. columns packed with Chromosorb-102. The integrated areas of chromatographic peaks were obtained using a Perkin Elmer M-2 calculating integrator coupled with the gas chromatographs.

Prior to each experimental run the desired wind speed was set by either removing or inserting the flow restrictor baffle, and the fences were fixed in place for wind fence experiments. The water tank was partially filled with tap water, then a charge of ethyl ether was added. The charge gave an approximate concentration of 100 ppm. Water and ether were well mixed with a rod and the tank completely filled to level with additional water. The blower was started at this time and the level controller adjusted such that dyed water would barely enter the water tank. Several minutes after the blower was started readings of the air and water temperatures, the air velocity and water depth in the reservoir cylinder were taken. Samples of the water phase were then removed from the tank. Liquid was introduced into the sampling tube by inducing a siphon with a rubber bulb through a Vacutainer (TM) tube holder. Then the evacuated

Vacutainer (TM) sample vials were partly pushed into the tube holders. When all sample ports were ready each vial was completely thrust into the tube holder, puncturing the septum and causing sample to be drawn into the sample vial. The entire sampling process was completed in less than one minute for eight sample ports. The sample was not exposed to the atmosphere and a reproducible amount was withdrawn each time. The liquid sample was then analyzed by gas chromatograph. The sampling process was repeated at various time intervals until 60-80 percent of the chemical had desorbed from the water tank.

Assuming mass balance closure a plot of the natural logarithm of the ratio of the chemical concentration at time t and initial chemical concentration versus the passage of experimental time was made to determine the chemical desorption rate from the liquid phase (Thibodeaux, (1979). A least squares fit of the data yielded the desorption rate constant as the slope.

A total of 37 batch desorptions were performed with various fence arrangements around the water surface in the water tank. Two basic fence patterns were investigated. These were perimeter fences and network fences. A perimeter fence is one that encircles the impoundment at the water's edge. Network fences involve the installation of fences on (i.e. floating on piles) the water surface creating a series of uniformly spaced cells. These are shown schematically in Figure 6-3.

The degree of emission reduction is defined by

$$\text{Percent Reduction} = \frac{N_{w/o} - N_w}{N_{w/o}} \times 100 \qquad (6\text{-}4)$$

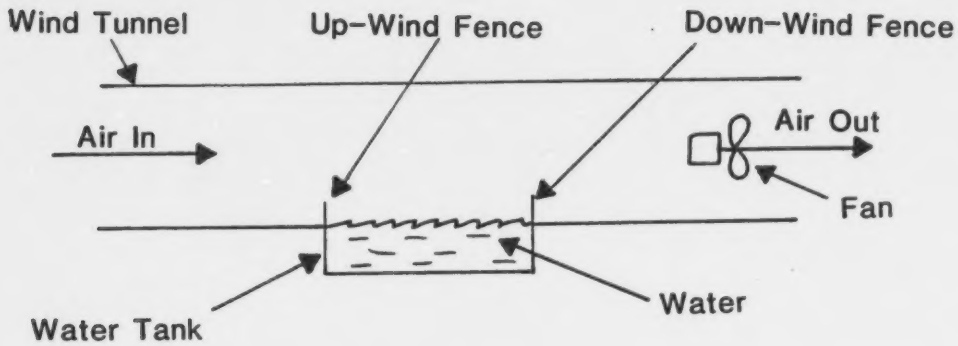
where $N_{w/o}$ and N_w are the emission rates without fences and with fences respectively. To nullify the effect of concentration, C_A was kept at zero or at $C_A/H < C_w$ in the inlet air at all times. Also the effect of C_w can be nullified by assuming identical values both with and without fences. Substituting equation (6-1) in (6-4) with the above conditions, yields

$$\text{Percent Reduction} = \frac{k\ (w/o) - k\ (w)}{k\ (w/o)} \times 100 \qquad (6\text{-}5)$$

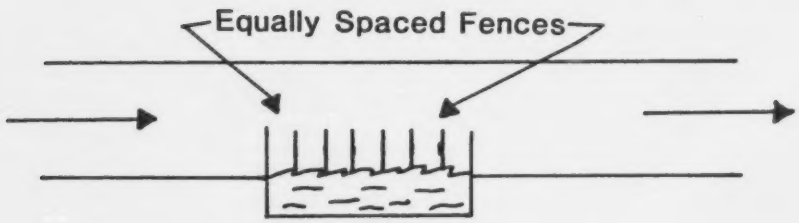
So it is possible to quantify the emission reduction potential of a particular fence arrangement by measuring k values.

The liquid phase coefficient without any type of fence in place was 3.424 cm/hr at V(10 cm) of 3.9 m/s and 2.375 cm/hr at V(10 cm) of 2.9 m/s. These results emphasize the importance of the velocity on the liquid phase mass transfer coefficient.

With fences mounted on the tank edge, simulating perimeter fences, several qualitative differences were noted regarding the level controller box and make-up water flow into the tank. The level controller box had to be raised, above its previous plane such that its outlet was above the tank inlet, to equalize the pressure heads. This indicates that the pressure leeward of the fence was less than the wind pressure exerted on the water when a fence was not present. The other qualitative difference observed was a change in direction of make-up water flow. Without fences in place make-up water flowed in the direction of the wind. With solid perimeter fences make-up water flowed in the direction opposite the mainstream wind flow. The existence of a recirculating eddy could cause this phenomenon by exerting a shear stress on the water surface. The



(A) PERIMETER FENCE PATTERN



(B) NETWORK FENCE PATTERN

Figure 6-3: Fence Arrangements on Water Surface

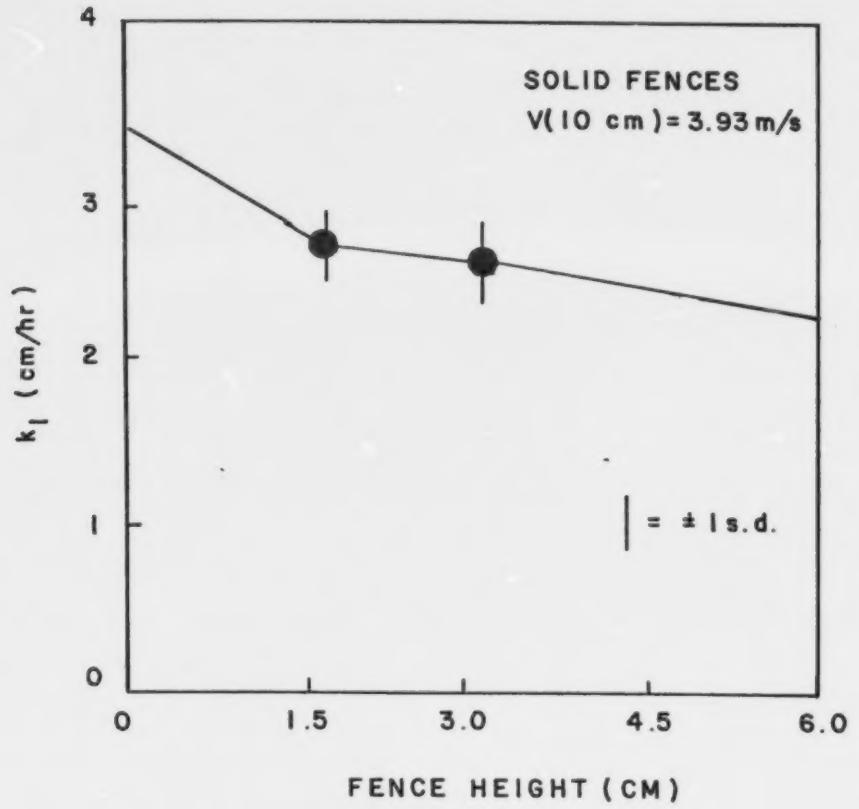


Figure 6-4: Liquid Phase Mass Transfer Coefficient versus Fence Height

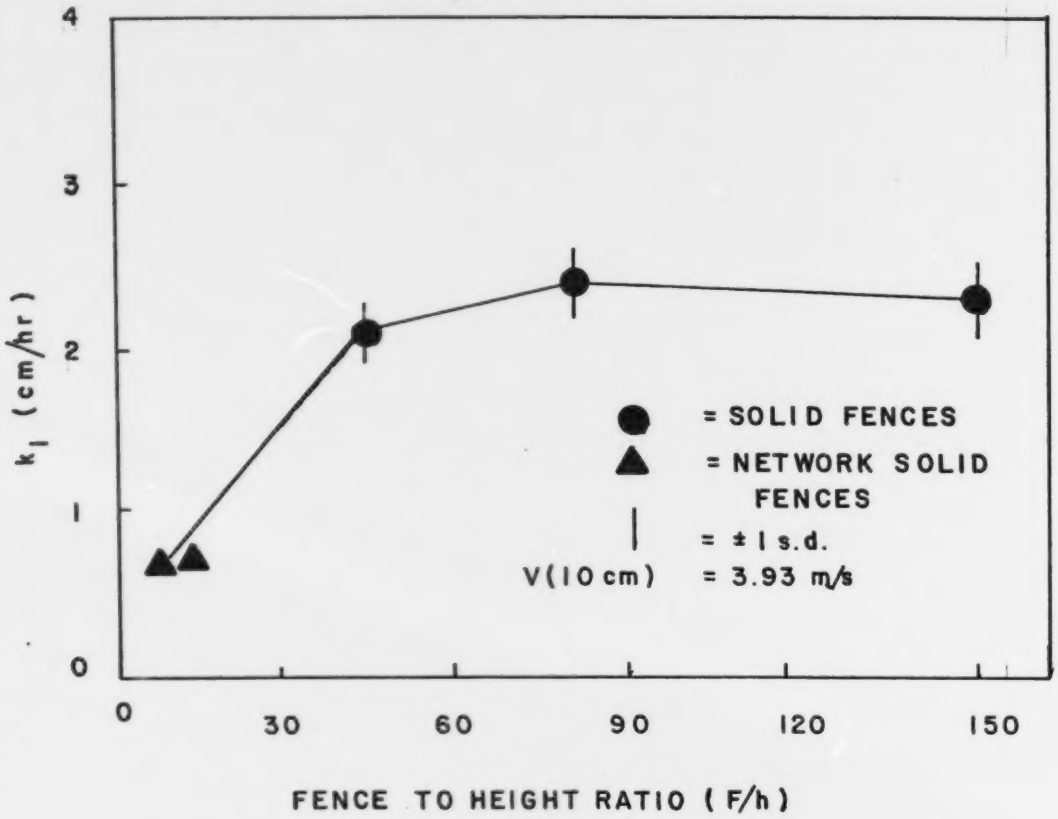


Figure 6-5: Liquid Phase Mass Transfer Coefficient versus (F/h)

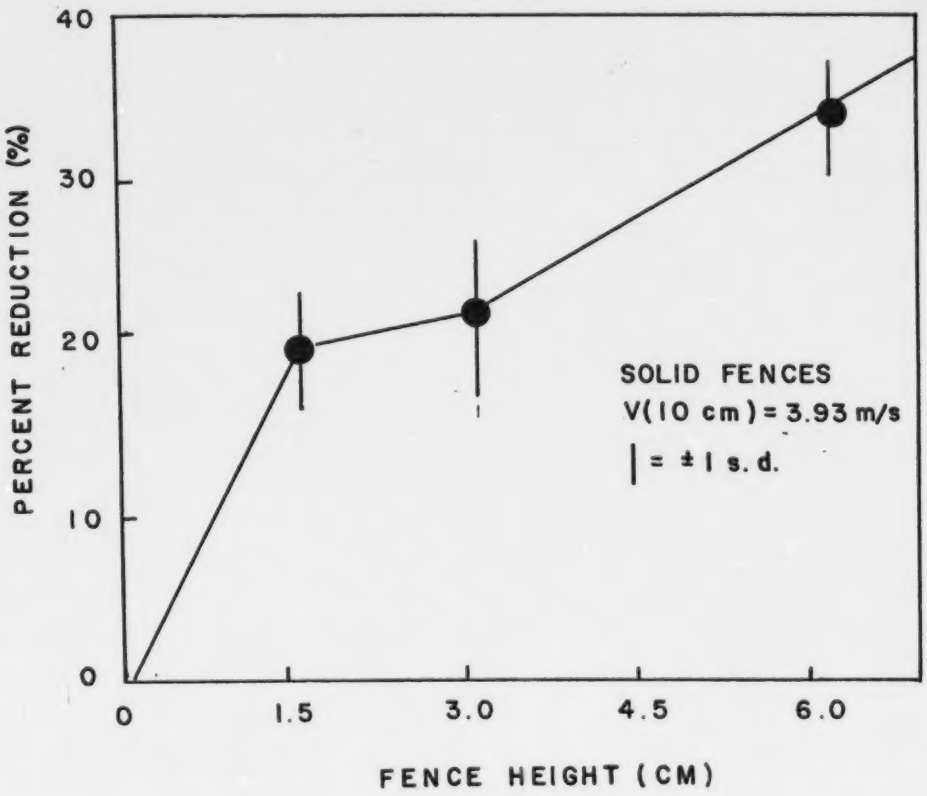


Figure 6-6: VOC Control versus Fence Height

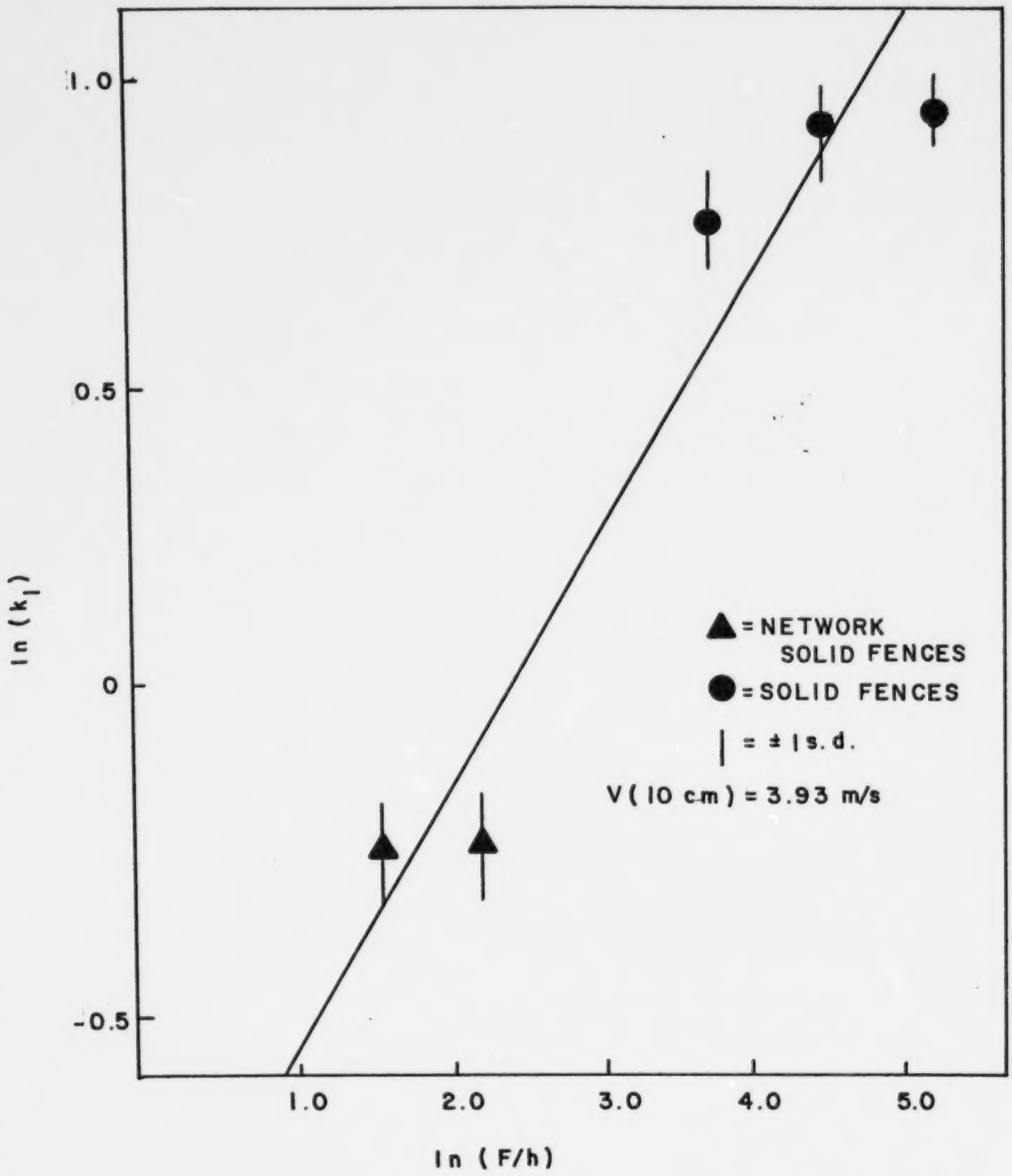


Figure 6-7: Log Plot of Liquid Phase Coefficient versus (F/h)

taller fences increased the windward velocity measured at 10 cm height. Thus, deflection flow or a windward recirculating eddy was generated by the fences. Qualitatively, complex flow leeward of the fences was indicated by these phenomena.

Concentration differences in the water tank with respect to position was an initial concern because of the complex flow patterns leeward of the fence. A statistical program using Statistical Application Series (SAS) (TM) to curve fit the concentrations measured at each sampling to a polynomial dependent on position was used to determine that this concern was not valid for this experimental system. Division of the water phase into compartments might have had a different result.

The installation of fences reduced the liquid phase mass transfer coefficient as listed in Table 6-2. The most significant reduction of 78 percent resulted from installment of the commercial wind fence material, DustTamer (TM), and networks of small solid fences. The DustTamer (TM), and networks were spaced at 5 and 10 heights with h(m) of 1.7 cm, h(L) of 1.2 m. The solid perimeter fences of model heights 6.4 cm, 3.2 cm, and 1.7 cm decreased the coefficient by 34.4 percent, 22.8 percent, and 19.7 percent respectively. Results at V(10cm) were quite variable. This is consistent with Lunney (1983) and Mackay (1978) who state that wind enhancement of the liquid phase mass transfer coefficient was not notable at V(10cm) of this magnitude.

Several experiments where the 6.4 cm model perimeter fence was angled leeward were performed to determine whether any benefit would be realized as indicated by snow fence design. At 80 degrees from the horizontal the resulting liquid phase mass transfer coefficient was within the experimental error of the perpendicularly erected fence. A 45 degree angle afforded less reduction than the projected height of the angled fence.

Figures 6-4, 6-5, and 6-6 show the parabolic relationships between the liquid phase mass transfer coefficient and fence height and fetch to fence height ratio and percent VOC emission reduction and fence height. These types of curves are expected since there is a limit to the reduction a wind fence could offer.

Figure 6-7 shows the results of a plot of the natural logarithm of the liquid phase mass transfer coefficient versus the natural logarithm of the fetch to fence height ratio (F/h). The line has a slope of 0.4619 and a correlation coefficient of 0.9513 as calculated by linear regression. The liquid phase mass transfer coefficient could be expressed as:

$$k_\ell = 0.328\left(\frac{F}{h}\right)^{0.4619} \qquad (6\text{-}6)$$

Thus, the coefficient varies as the reciprocal of h raised to the 0.4619 power, which is very similar to results predicted by the modification of Levich's theoretical development of the problem (equation 6-3). Appropriateness of scaling fence height to lagoon fetch is indicated by this correlation.

If the plot were extended to intersect with the line y=ln(3.424) the limiting (F/h) ratio would be obtained. Above this ratio a fence would have a negligible effect on the liquid phase mass transfer coefficient. The limiting fetch to fence height ratio is 160. Taller fences or fence networks to compart-

TABLE 6-2

FENCE CONTROL SIMULATION RESULST AT V = 3.9 m/s AND V = 2.9 m/s

Results: Corrected to 293K

	Fence height (cm)	k_1 (cm/hr)	s.d	Reduction (%)
	V(10 cm) = 3.9 m/s			
No Fence	0.0	3.424	0.039	0.0
Perimeter Fence				
Solid:				
90 deg.	1.7	2.750	0.224	19.7
	3.2	2.642	0.406	22.8
	6.4	2.251	0.160	34.3
80 deg.	6.4	2.087	0.085	39.1
45 deg.	6.4	3.211	0.134	6.2
Porous:				
90 deg.	6.4	0.7445	0.119	78.3
Solid Fence Networks:				
5 h	1.7	0.7328	0.0908	78.6
10 h	1.7	0.7540	0.0454	78.0
	V(10 cm) = 2.9 m/s			
No Fence	0.0	2.375	0.333	0.0
Perimeter Fence				
Solid:				
90 deg.	1.7	1.403	0.460	40.9
	3.2	1.893	0.673	20.3

mentalize the water surface would be a consideration for existing lagoons with large fetches.

The performance of the commercial (porous) wind fence material was unexpected. The 80 percent reduction in the liquid phase mass transfer coefficient closely parallels the reduction obtained in fugitive dust control studies (Drehmel et al., 1982). This result may be attributed to the lesser degree of turbulence intensity leeward of a porous fence. Raine and Stevenson (1977) deduce from data that turbulence intensity and eddy length scale decrease with the size of openings in the wind fence. The eddy length scale becomes smaller than fence height at a geometric porosity greater than 35 to 50 percent. The commercial wind fence material had small openings afforded by the industrial polyester threads. The porous wind fence leeward flow would have small scale turbulence and expanded shelter zone, but less mean velocity reduction.

Using equation (6-6) for k (w) in equation (6-5) yields

$$\text{Percent Reduction} = 1 - 0.096\left(\frac{F}{h}\right)^{0.462} \qquad (6\text{-}7)$$

for $1.6 < \frac{F}{h} < 160$. Thus data in Table 6.2 and Figure 6-7 (which is a plot for the 90° solid perimeter and network fence data) suggest that very little reduction is achieved for fence spacings of 160 or greater. Therefore percent reduction = 0 for (F/h) greater than 160 completes the design equation. It should be noted that this equation is only valid for chemicals that are liquid-phase controlled (most of the volatile chemicals happen to be so).

6.1 Conclusions

The overwhelming conclusion is that wind fences do decrease the wind enhanced liquid phase mass transfer coefficient in all manners of application. The rest of the conclusions follow:

(1) Each of the five wind fence arrangements decreased the liquid phase mass transfer coefficient. The fence networks and the porous fence outperformed the other arrangements and materials.

(2) For solid fences over simulated lagoons at a wind velocity of 3.93 m/s the liquid phase mass transfer coefficient was very nearly proportional to the square root of the ratio of lagoon fetch (F) to fence height.

(3) Lagoon fetch appears to be a valid parameter for scaling wind fences to control emissions of volatile chemicals.

(4) Based on laboratory simulations, at a (F/h) greater than 160 a wind fence is not expected to have much influence on the liquid phase mass transfer coefficient.

(5) Laboratory simulations using ethyl ether in a wind tunnel, water tank device yielded significant emission reductions. A perimeter fence of solid construction (i.e, non-porous) can give up to approximately 40% volatile reduction. A network grid can give up to 80% reductions as can a porous perimeter fence as a means of emission reduction.

If there are no competitive pathways for the fate of the volatiles in the impoundment such as biochemical degradation, hydrolysis, photolytic degradation, etc. then the use of fences will not reduce the quantity of volatiles ultimately emitted to the atmosphere. On the other hand, the wind fences will reduce the rate of emissions of the VOCs. If other degradation mechanisms are present within the impoundment, the presence of wind fences will increase the residence time for the VOCs in water and would therefore help in the efficient destruction or conversion reactions. It is unlikely that wind fences would prove to be of any effect at all under periods of low wind or no-wind conditions in operating conditions when the water is warmer than the air above. Under these thermal conditions the VOC will diffuse away from the surface in a vertical direction. In this case, the transport mechanism is one of natural convection due to warm, humid air rising from the water surface. These situations are handled in the next section.

7.0 FLOATING OIL COVERS AND SURFACTANTS

Most of the control strategies in the previous sections (except the one on aerodynamic modifications) have dealt with controlling VOC emissions from impoundments without affecting the mass transfer processes occurring either in the liquid or air phases of the air-water interface existing in a surface impoundment.

The process of volatilization is a first order phenomena and is represented by the following equation

$$N = K (C_W - C_A/H) \qquad (7\text{-}1)$$

where N is the emission flux rate of chemical A, $kg/m^2.s$
K is the overall mass transfer coefficient, m/s.
C_W is the concentration of the volatile species in water, kg/m^3
C_A is the concentration of the volatile species in air, kg/m^3
H is the Henry's constant for the volatile species in m^3 water per m^3 air.

The overall mass transfer coefficient, K is related to the individual mass transfer coefficients k_ℓ and k_g for the liquid and gas phases respectively as follows

$$\frac{1}{K} = \frac{1}{k_\ell} + \frac{1}{k_g H} \qquad (7\text{-}2)$$

The term $1/k_\ell$ gives the liquid side resistance and $1/k_gH$, the gas side resistance. For most chemicals of interest $k_gH > k_\ell$ and hence the process of volatilization is said to be liquid phase controlled. Both k_ℓ and k_g incorporates mechanical and nature stimulated events.

In the previous section the effect of wind upon k_ℓ was explored. Wind effects both k_ℓ and k_g; k_ℓ increases with the square of wind velocity while kg increases proportional to wind velocity. In the absence of wind the temperature difference between the water and air is the important variable (Springer et al., 1985; Springer et al., 1984). If the water is warmer than air then both k_ℓ and k_g are proportional to $T^{1/4}$.

Inspection of equation (7-1) shows that a reduction in emission can be obtained by two ways:

(i) By decreasing the concentration of the volatile in the liquid phase and

(ii) By reducing the value of K, the overall mass transfer coefficient

For a given concentration level of the volatile in water, reducing K may be the most effective way of reducing the emission rate. A decrease in K can be brought about by adding additional resistances at the interphase. The technique of adding immiscible oil covers provides just the same effect. In this section we describe our experimental results on the use of oil covers to

reduce volatile emissions, both under conditions of no-wind over the surface and under highly windy conditions. We also review the use of surfactants at the air-water interface as a control option.

7.1 Oil Cover - No-Wind Conditions

It has been observed that in the absence of significant wind, the single most important parameter which controls the volatilization from surface impoundments is the temperature difference between water and air (Springer et al., 1985). A worst case scenario for a nowind condition would be a situation where the water is warmer than the air. In practice such situations can occur when the impoundment liquid warms up during the daytime and towards evening when the sun no longer heats up the liquid, the natural convection process tends to cool the water; this then becomes the dominating process for VOC emissions. This particular situation which we studied will be covered in this section.

In the absence of wind, a very thin layer of immiscible organic (oil) will completely cover the surface of an impoundment. Generally, the minimum thickness of a complete layer will depend upon the interfacial tension and the density of the oil; below some critical amount, the organic layer of oil will collect itself into the so called "lenses" which will not completely cover the surface. These "lenses" are in equilibrium with a monomolecular film of the material and their behavior has been the subject of much study in Surface Chemistry (Adamson, 1982). Such configurations are extremely sensitive to both temperature and concentration gradients on the surface and in the bulk solution, and would eventually lead to the so called "interfacial turbulence" (Levich, 1962).

When the surface is uniformly covered (without any "lenses") we can use a "three-resistance model" to describe the mass transfer coefficient (See Figure 7-1 for the various corresponding interfaces in the control system). This was derived by Nguyen (1984) and is given below.

$$\frac{1}{K_W} = \frac{1}{k_w} + \frac{1}{\pi k_o} + \frac{1}{H k_g} \qquad (7\text{-}3)$$

where K_W = overall liquid (water) phase mass transfer coefficient, m/s
k_w = individual liquid (water) phase mass transfer coefficient, m/s
k_o = individual oil phase mass transfer coefficient, m/s
k_g = individual gas phase mass transfer coefficient, m/s
π = partition coefficient for the VOC between oil and water (dimensionless)
H = Henry's law constant for the VOC between air and water (concentration units ratio, dimensionless).

The three reciprocals on the right side of equation (7-3) each represent a resistance; the first term gives the water phase resistance and the third term gives the gas phase resistance. Previous results (Springer et al., 1984, 1985) indicate that the third term, $1/Hk_g$ is negligible in comparison to the other terms for most liquid phase controlled chemicals of environmental significance. The first term $1/k_w$ is of the same order of magnitude for most VOCs, since according to traditional mass transfer theory, the value of

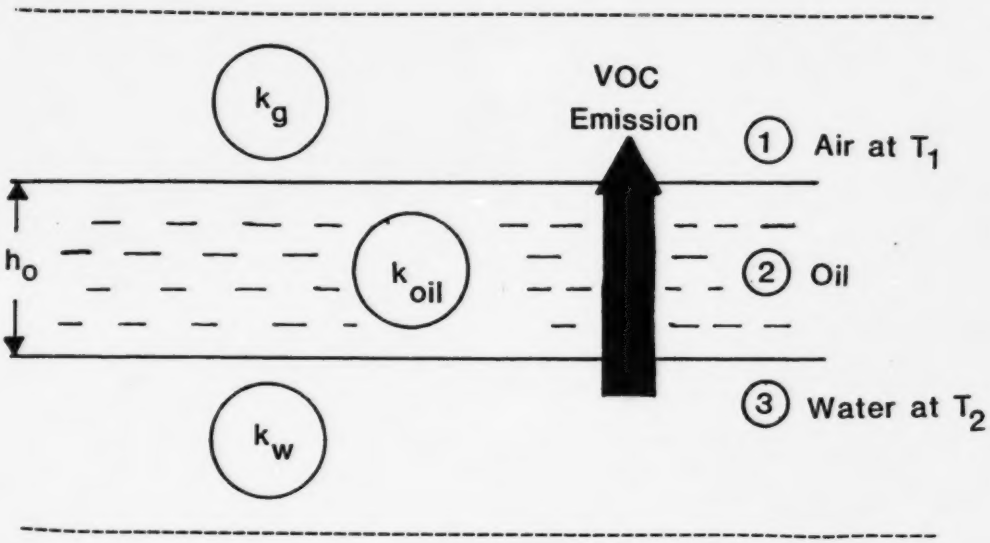


Figure 7-1: Interfaces in the Control System -- $T_2 > T_1$

k_w from one chemical to another varies only as the two thirds power of diffusivity. Therefore, the term $1/\pi k_o$ decides the effectiveness of the method as a control option.

We would anticipate that the value of k_o would also be similar in magnitude for many of the VOCs, because it too would vary from one chemical to another only because of variations in diffusivity of the chemical in the oil. Hence, the value of the partition coefficient π becomes all important. The greater the solubility of the chemical in the oil, the greater is the value of π. This means the oil phase resistance term decreases in value and hence the less effective is the oil cover with regard to the value of k_o. One can make a crude approximation that

$$k_o \simeq \frac{D_o}{h} \qquad (7\text{-}4)$$

where D_o = diffusivity of the VOC in oil, m^2/s
h = thickness of the oil layer, m

Then, to a first approximation we can expect that k_o decreases as h increases; i.e., the oil layer will become more effective as its thickness increases, which confirms our intuition.

This chemodynamic model thus predicts better reduction in VOC air emissions for greater depth of oil layers and for chemicals with low partition coefficient (low oil solubility).

Since correlations for liquid phase mass transfer coefficients for a non-aqueous phase are not available we did not compare our experimental results with those predicted by the model, but we checked the two qualitative predictions of our model described in the previous paragraph. A comparison was tried but didn't prove adequate nor justifiable (Valsaraj et al., 1985)

The experimental arrangement which was used for this purpose was described extensively by Nguyen (1984). The impoundment simulator consisted of a circular tank 1.83m in diameter and 0.61m deep. It was insulated on the bottom and sides with about 0.15m of polystyrene foam insulation. The apparatus was located indoors and to further shield the apparatus from stray air currents, it was surrounded by an enclosure made of polyethylene film which was approximately 4.8m x 4.8m x 2.4m high open at the top. A cut-away view of the apparatus is shown in Figure 7-2. The temperature profiles in the liquid and air phases were monitored using thermocouples mounted on a standard in the center of the tank. The liquid was heated to approximately 40·C using a heat transfer coil (removable). We thus simulated the worst-case conditions for a no-wind situation, i.e., with the impoundment liquid warmer than the air.

With the idea of studying the natural convection process wherein the liquid phase was cooled from its surface, we felt it quite important that there be no additional heating of the liquid phase during the measurements since this would introduce additional convection currents. Thus, it was a necessary condition that the temperature of the liquid phase would change during the course of the experiment. Since it was considered inappropriate

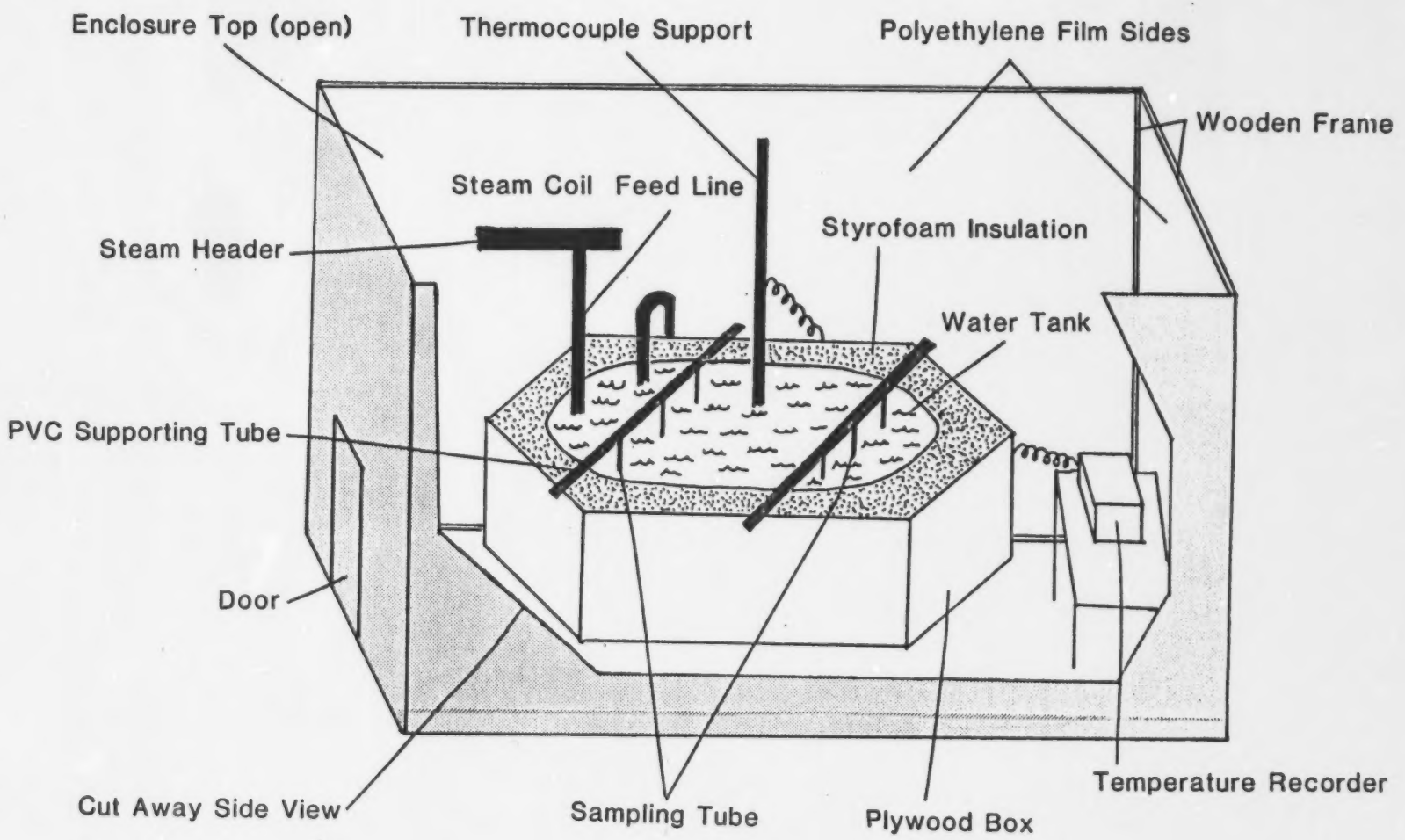


Figure 7-2: Simulator for Surface Impoundment Under No-Wind Condition

to try to maintain a constant gas phase temperature (to do so would require an undesired enhancement of circulation in the gas phase), the gas phase temperature also changed during the course of the experiment. Finally, to determine the rate of emission it was decided to monitor the rate of change of liquid phase concentration with time, since collecting gas samples would have completely overridden the gas phase convection process under study.

An experimental determination began by filling the simulator with water and warming up to 40-42°C using a submerged steam coil. The coil was then removed and approximately 400 ml of the VOCs were stirred in. The oil layer was then added by simply pouring in the oil. The VOCs used in these experiments and their properties are listed in Table 7-1. Three types of oil covers were used, viz., mineral oil, 1-octanol and lauryl alcohol. The mineral oil had a viscosity of 52±1.5cP at 25°C and the molecular weight was estimated to be 200±30 from information supplied by the manufacturer.

Approximately an hour was allowed for the currents induced by stirring to subside. Aqueous samples (5ml.) were then withdrawn at appropriate time intervals into Vacutainer sampling tubes supplied by Becton-Dickinson and Company. The concentration of VOCs in the samples were analyzed using a Perkin-Elmer Sigma 3 gas chromatograph or a Tracor 565 gas chromatograph both equipped with Flame Ionization detectors and using 6 ft. long, 1/8 inch i.d. steed column packed with Chromosorb 102. Chromotographic peak areas were calculated using either a Perkin-Elmer M-2 calculating integrator or a Hewlett Packard 3392A integrator.

Three different materials were used as the cover, namely, mineral oil, n-octanol and n-dodecanol (lauryl alcohol). Mineral oil was chosen because it had properties similar to petroleum products which are commonly found to float on surface impoundments. The mineral oil we chose was a commercial sample and its properties left much to be desired. In order to provide for a better range of properties like solubility of VOC in the cover and also the miscibility (solubility) of the oil cover in water we chose octanol and lauryl alcohol also for experimentation.

The results for the mineral oil cover for the VOC emission reductions of benzene, acetone and n-propanol are given in Table 7-2. The desorption rates are shown in Figures 7-3, 7-4 and 7-5. For octanol and lauryl alcohol only acetone was used as the VOC in aqueous solutions. The results are shown in Table 7-3 and in Figures 7-6 and 7-7.

The degree of emission reduction is defined by

$$\text{Emission reduction} = \frac{N_{w/o} - N_w}{N_{w/o}} \qquad (7\text{-}5)$$

where $N_{w/o}$ and N_w are the emission rates without and with oil cover respectively. To nullify the effect of concentration C_A was kept negligibly small and C_w was assumed identical. Then using equation (7-1) in (7-5) we can write

$$\text{Emission reduction} = \frac{K_{w/o} - K_w}{K_{w/o}} \qquad (7\text{-}6)$$

Table 7-1. Chemical Properties of Experimental VOCs

Chemical	Diffusivity in oil[1] (cm^2/s)	Partition Coefficient[2]	Diffusivity in water[3] (cm^2/s)	Henry's Law Constant[4]
Benzene	4.1×10^{-7}	~ 130	1.02×10^{-5}	0.4
Acetone	4.5×10^{-7}	~ 1	1.12×10^{-5}	0.004
n-propanol	4.6×10^{-7}	~ 1	1.16×10^{-5}	0.001

(1) Diffusivity in oil was assumed to be a constant factor (0.04) times the diffusivity in water.

(2) Partition coefficients experimentally mesured. (For details see Nguyen (1984)

(3) Water phase diffusivities estimated at 25·C (For details see Nguyen (1984)

(4) Henry's Law constant is a concentration units ratio (Thibodeaux, 1979).

Table 7-2. Fractional Reduction in Emissions Using Various Mineral Oil Layer Thicknesses

Oil Thickness (cm)	Temp. Ranges, ·K		Fractional Reduction [1]		
	Air	Water	Benzene	Acetone	n-propanol
0.20	303-309	320-318	0±	0.35	0.38
0.27	300-306	321-318	0.10	0.43	0.60
0.30	303-304	319-317	0.32	0.70	0.58
0.46	303-304	319-317	0.53	0.68	0.69

(1) A reliable estimate of experimental error is not possible since values for estimating coefficients are deduced from slopes of transformed data (figures attached). Depth of the water in the impoundment in all cases was 0.49m. The thickness values can be converted into volume by multiplying them with the area of the impoundment (2.63 sq. m.)

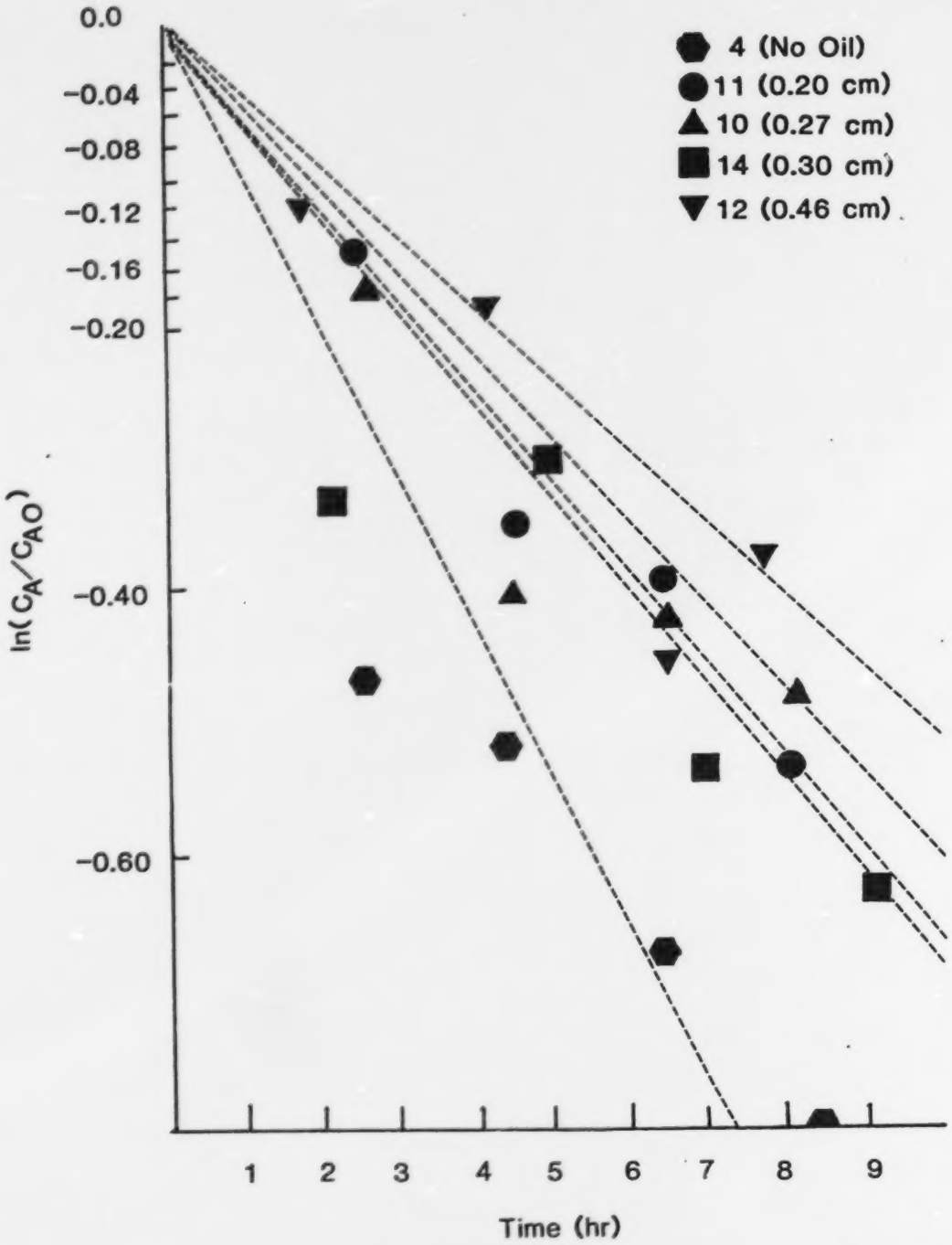


Figure 7-3: Experimental Results for Benzene Under Different Mineral Oil Thicknesses

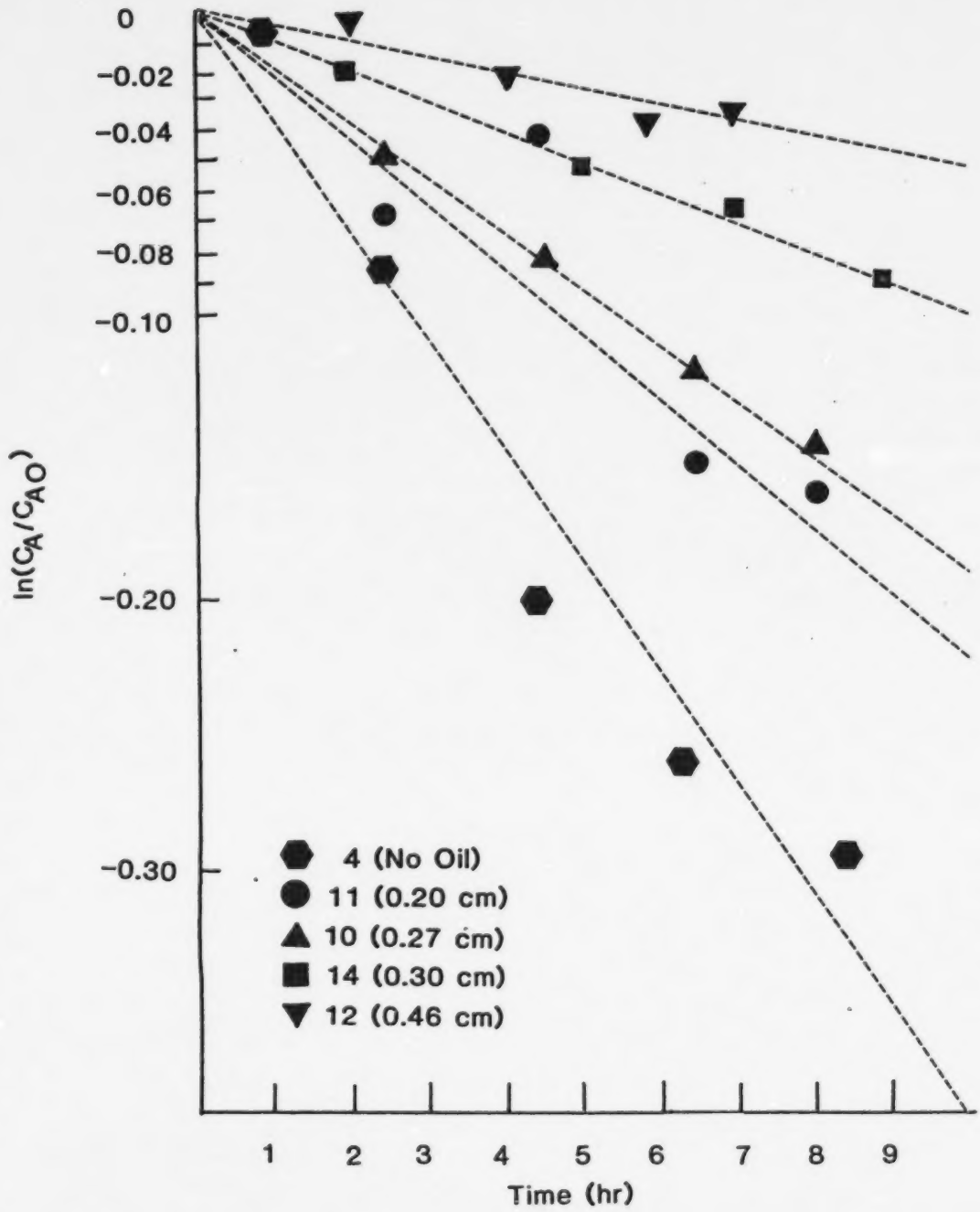


Figure 7-4: Experimental Results for Acetone Under Different Mineral Oil Thicknesses

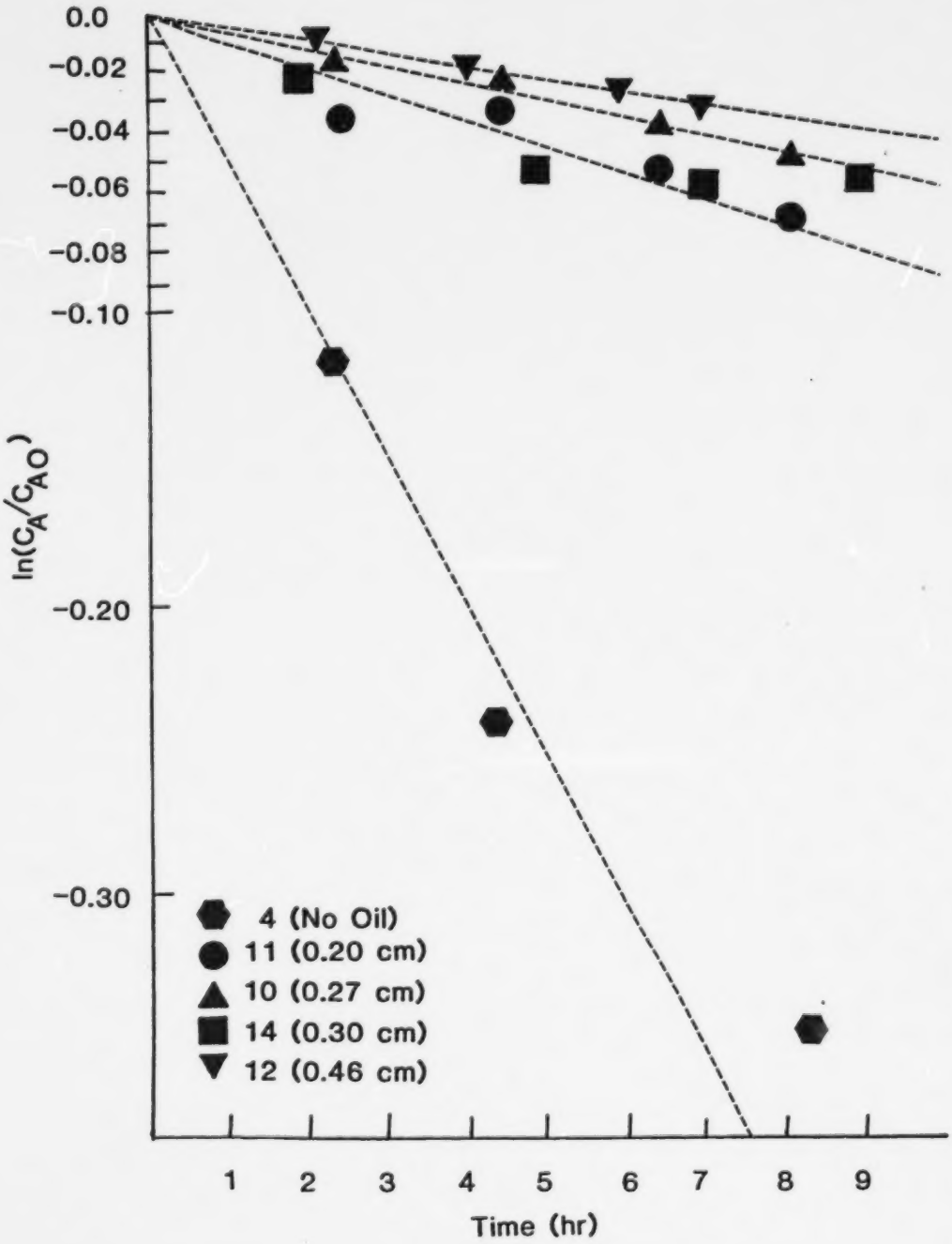


Figure 7-5: Experimental Results for n-Propanol Under Different Mineral Oil Thicknesses

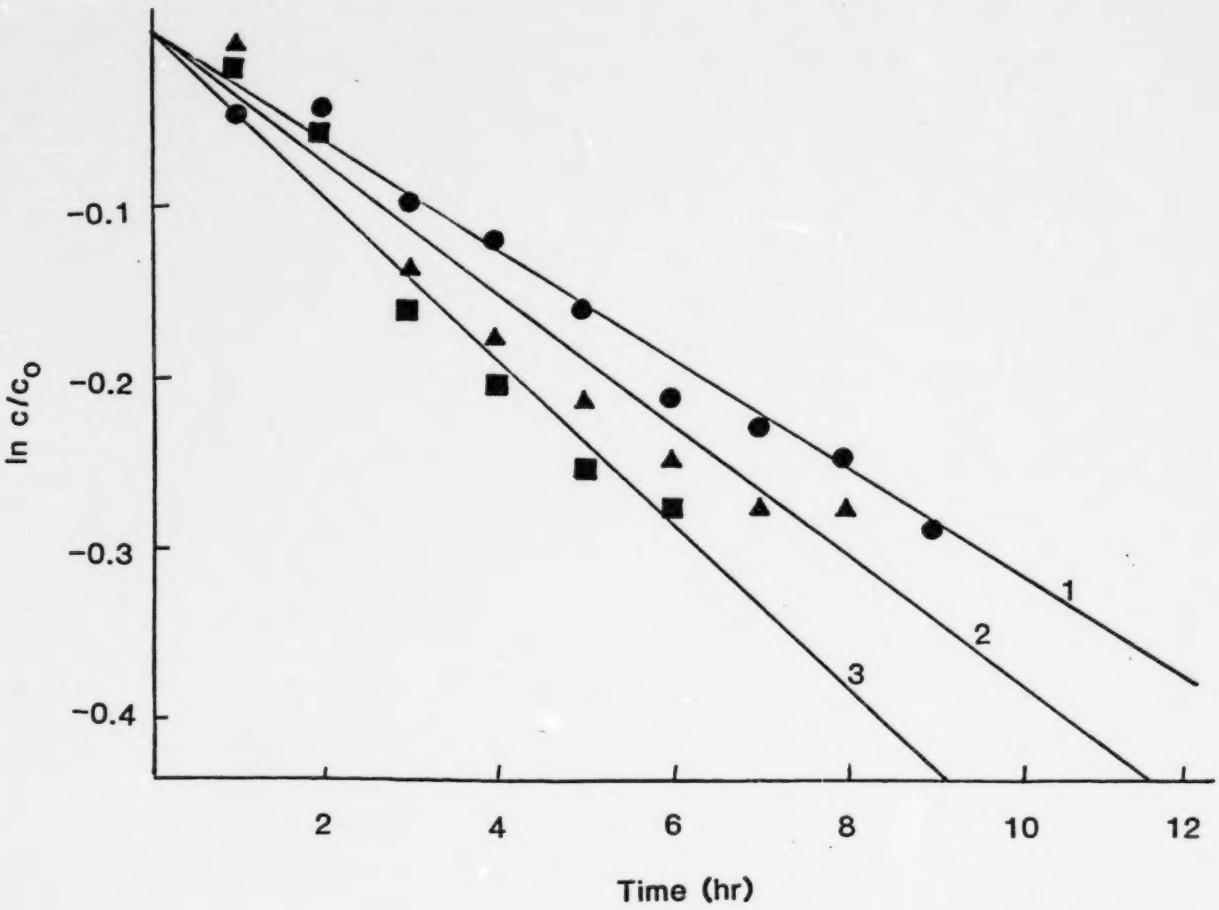
Table 7-3. Emission Reduction for Acetone Using Octyl Alcohol and Lauryl Alcohol as Immiscible Covers

	Temp. Range °K		Thickness (cm)	Fraction of Surface Covered (%)	Fractional Emission Reduction
	T_{Air}	T_{Water}			
Octyl alcohol (partition coefficient, $\pi = 1.9$)**	302-301	319-309	-	10	-0.21
	301-303	318-311	-	40	-0.77
	298-302	320-309	0.11*	80	0.07
	298-301	319-312	0.17*	95	0.50
	302-301	322-317	0.35	100	0.67
	299-303	320-316	0.47	100	0.87
Lauryl alcohol (partition coefficient, $\pi = 0.53$)**	296-298	317-307	0.01*	5	-0.12
	294-300	317-308	0.025*	20	0.11
	294-295	317-309	0.075*	50	0.55
	296-295	318-313	0.34	100	0.91
	295-297	318-313	0.36	100	0.93
	298-296	318-313	0.48	100	0.95
	298-294	318-313	0.55	100	0.96

*These thickness values represent the equivalent thickness of the layer had it spread so as to cover the whole surface. Surface coverage fractions are visual estimates. The thickness values can be converted into volume by multiplying them with the area of the impoundment ($2.63 m^2$).

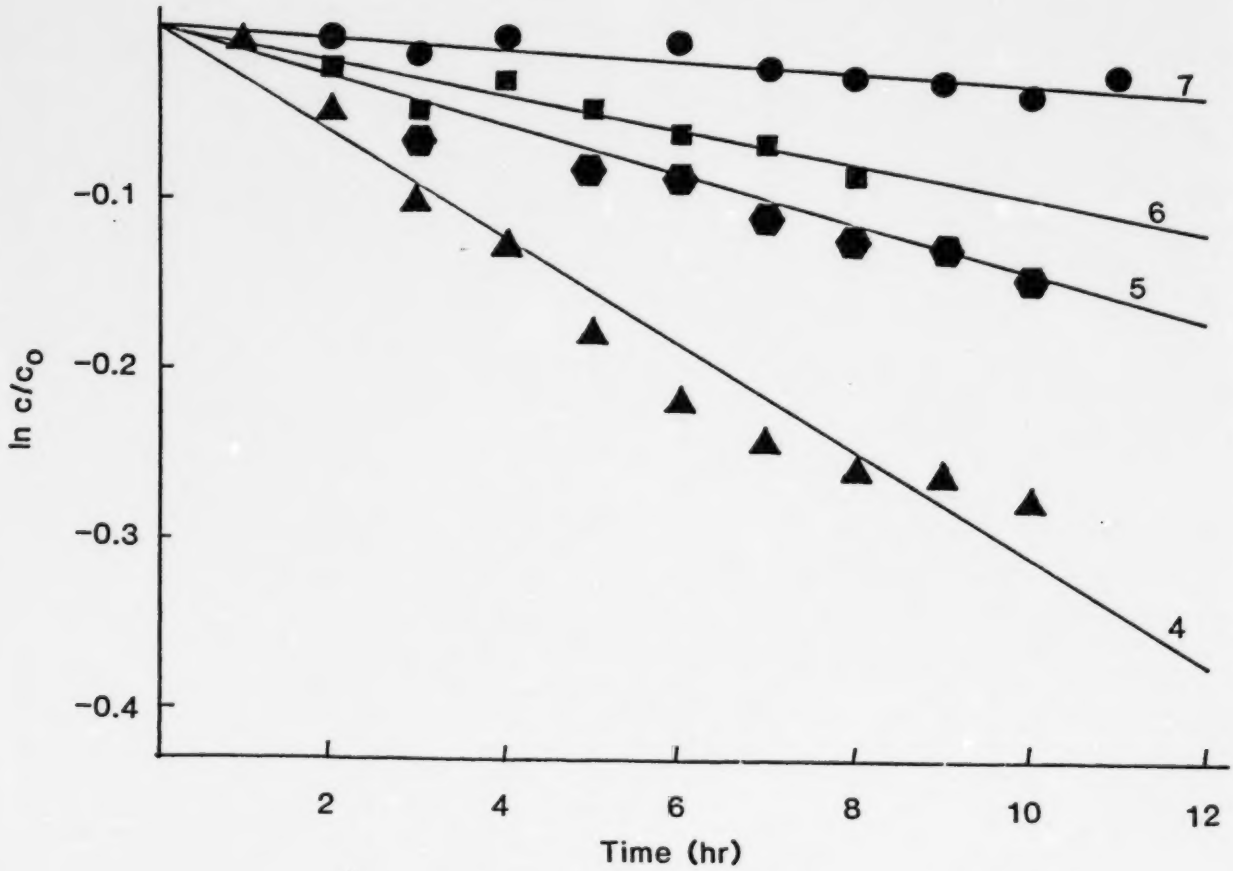
**Partition coefficients were measured using the procedure described by Nguyen (1984).

***Temperature ranges are over a twelve hour duration of experiments.



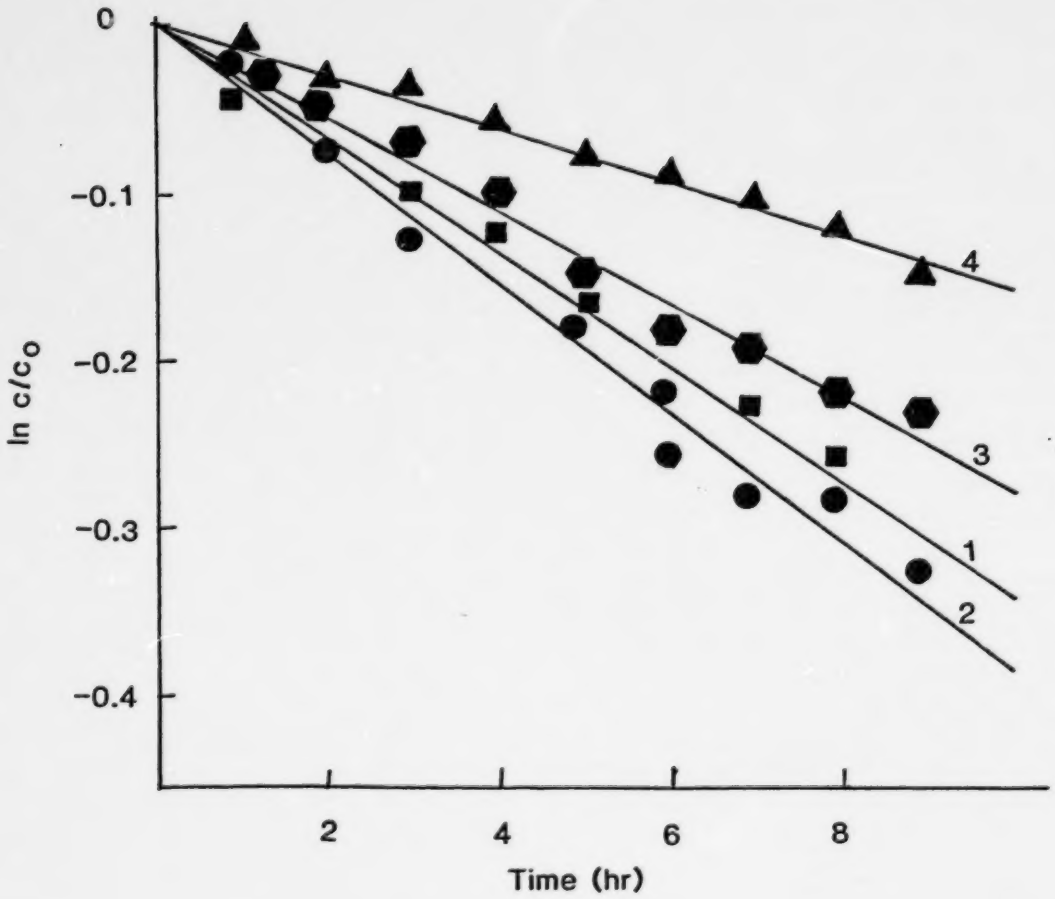
	KEY	SLOPE	CORRELATION	% COVERAGE
RUN 1	●	0.0328	0.9876	0
RUN 2	▲	0.0378	0.9650	10
RUN 3	■	0.0582	0.9793	40

Figure 7-6(a): Experimental Results for Acetone Desorption Under Octanol Cover (Surface Partially Covered)



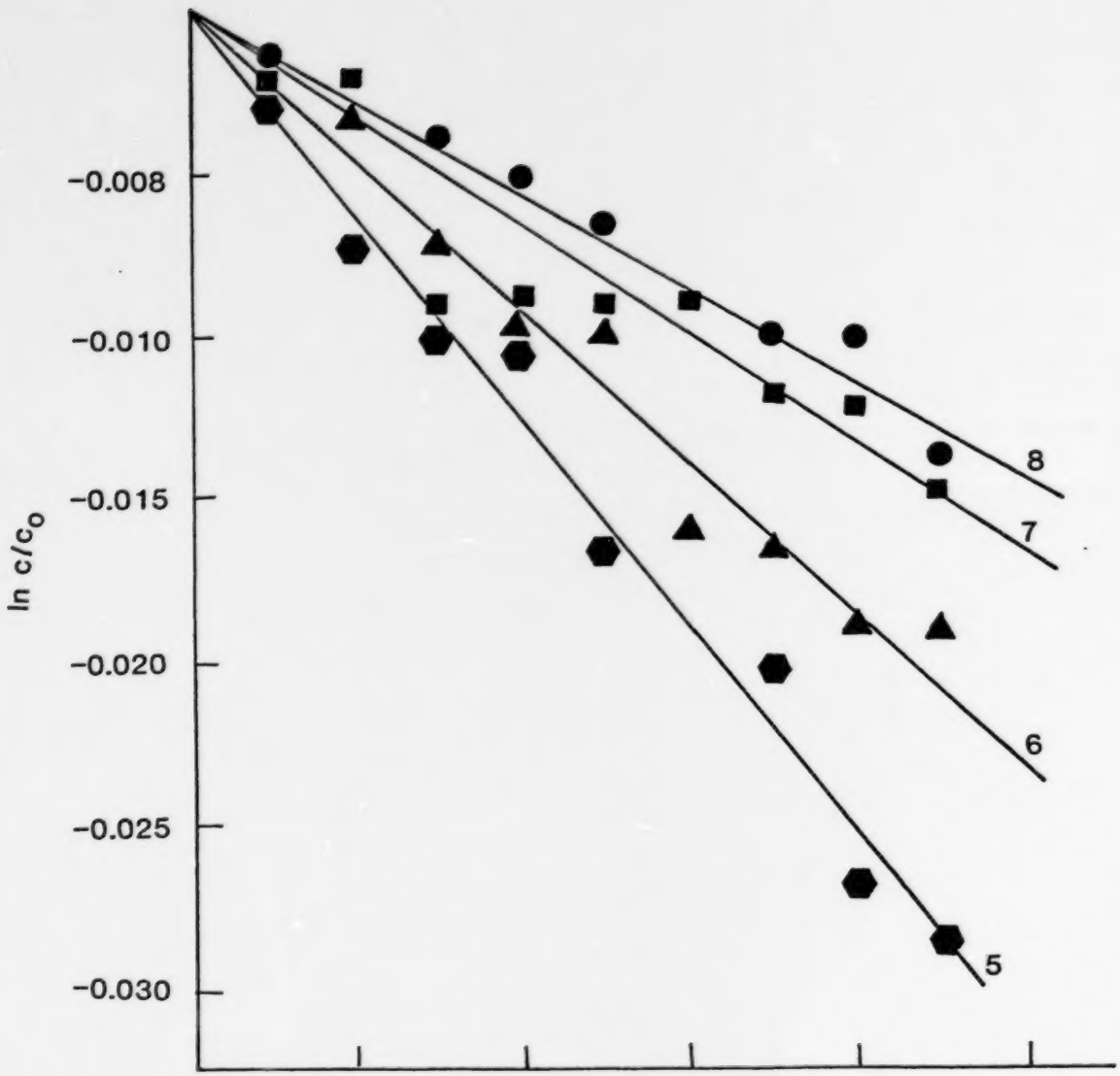
	KEY	SLOPE	CORRELATION	% COVERAGE	THICKNESS
RUN 4	▲	0.0305	0.9761	80	0.11 cm
RUN 5	⬢	0.0162	0.9904	95	0.17 cm
RUN 6	■	0.0109	0.9109	100	0.35 cm
RUN 7	●	0.00424	0.9006	100	0.47 cm

Figure 7-6(b): Experimental Results for Acetone Desorption Under Octanol Cover (Surface Almost to Fully Covered)



	KEY	SLOPE	CORRELATION	% COVERAGE
RUN 1	■	-0.03288	0.9876	0
RUN 2	●	-0.03686	0.9771	5
RUN 3	⬢	-0.02595	0.9868	20
RUN 4	▲	-0.01479	0.9874	50

Figure 7-7(a): Experimental Results for Acetone Desorption Under Lauryl Alcohol Cover (Surface Only Partially Covered)



	KEY	SLOPE	CORRELATION	% COVERAGE	THICKNESS
RUN 5	⬢	-0.003164	0.9899	100	0.34 cm
RUN 6	▲	-0.002326	0.9828	100	0.36 cm
RUN 7	■	-0.001650	0.9925	100	0.48 cm
RUN 8	●	-0.001460	0.9811	100	0.55 cm

Figure 7-7(b): Experimental Results for Acetone Desorption Under Lauryl Alcohol Cover (Surface Completely Covered)

The K's in equation (7-6) are the experimental overall mass transfer coefficients. These are calculated from the slopes of the experimental plots of $\ln(C/C_o)$ versus time where C is the VOC concentration at time t in the aqueous phase and C_o is the initial concentration. The slope of such a plot was related to the mass transfer coefficient (see Springer et. al. 1984) as follows:

$$K = (\text{slope})(\text{depth of the impoundment}) \qquad (7\text{-}7)$$

A detailed description of the significance of $K_{w/o}$ was given earlier by Springer et al. (1984).

The results shown in Tables 7-2 and 7-3 as well as in Figure 7-7 confirm the qualitative predictions of the model with respect to the effect of the layer thickness of the cover and the value of the partition coefficient. The thicker the layer of covering liquid, the greater the fractional reduction in emissions. Furthermore, the lower the partition coefficient (see Table 7-1 and 7-2), the greater is the fractional reduction.

The percent VOC reductions for acetone, n-propanol and benzene are presented in Table 7.2. The percent reduction of each chemical is given as a function of the oil layer thickness. The temperature ranges of water and air are also included in the table. Also from Table 7.2, it is evident that the evaporations of acetone and n-propanol are better controlled by the oil layer than for benzene especially at lower thicknesses of mineral oil. For 0.46 cm of oil, the evaporations of acetone and n-propanol were reduced by 68% and 69%, respectively. However, with the same thickness of the oil layer, it shows only about 53% reduction for benzene.

Based on the properties of the chemicals, acetone and n-propanol are highly soluble in water and have very low oil solubility. They also display a small distribution coefficient between oil and water. It is believed that because of the low concentration gradients across the oil film for acetone and n-propanol, the chemicals would move through the oil film very slowly after reaching the water-oil interface from the bulk water. In this case, the desorption rates of acetone and n-propanol are controlled better by the oil phase. On the other hand, benzene is less soluble in water and have high oil solubility. The distribution coefficient for benzene is much larger than the coefficients of the two former chemicals. As expected, benzene moves through the oil film somewhat easier after reaching the water-oil interface. Because it is volatile, it would evaporate more readily when it moves to the oil-air interface. Overall, the results show that the emission rate of benzene is not very effectively controlled by the oil phase.

Examination of Figure 7-8 shows that even a very thin layer of lauryl alcohol will markedly reduce the acetone emission, and that thicker layers do not reduce the emissions in a linear manner. On the other hand, octanol, with which acetone has a higher partition coefficient, does not cause as high reduction in emissions and the fractional emission reduction has the appearance of being more nearly linear with thickness. We should expect a plot of fractional emission reduction versus thickness to approach unity (complete control) asymptotically at high values of cover thickness. Such is seen to be the case for acetone with lauryl alcohol (with low partition coefficient). For less effective control (higher partition coefficients) using octanol or mineral oil, we are able to observe only the lower, nearly linear end of the curve.

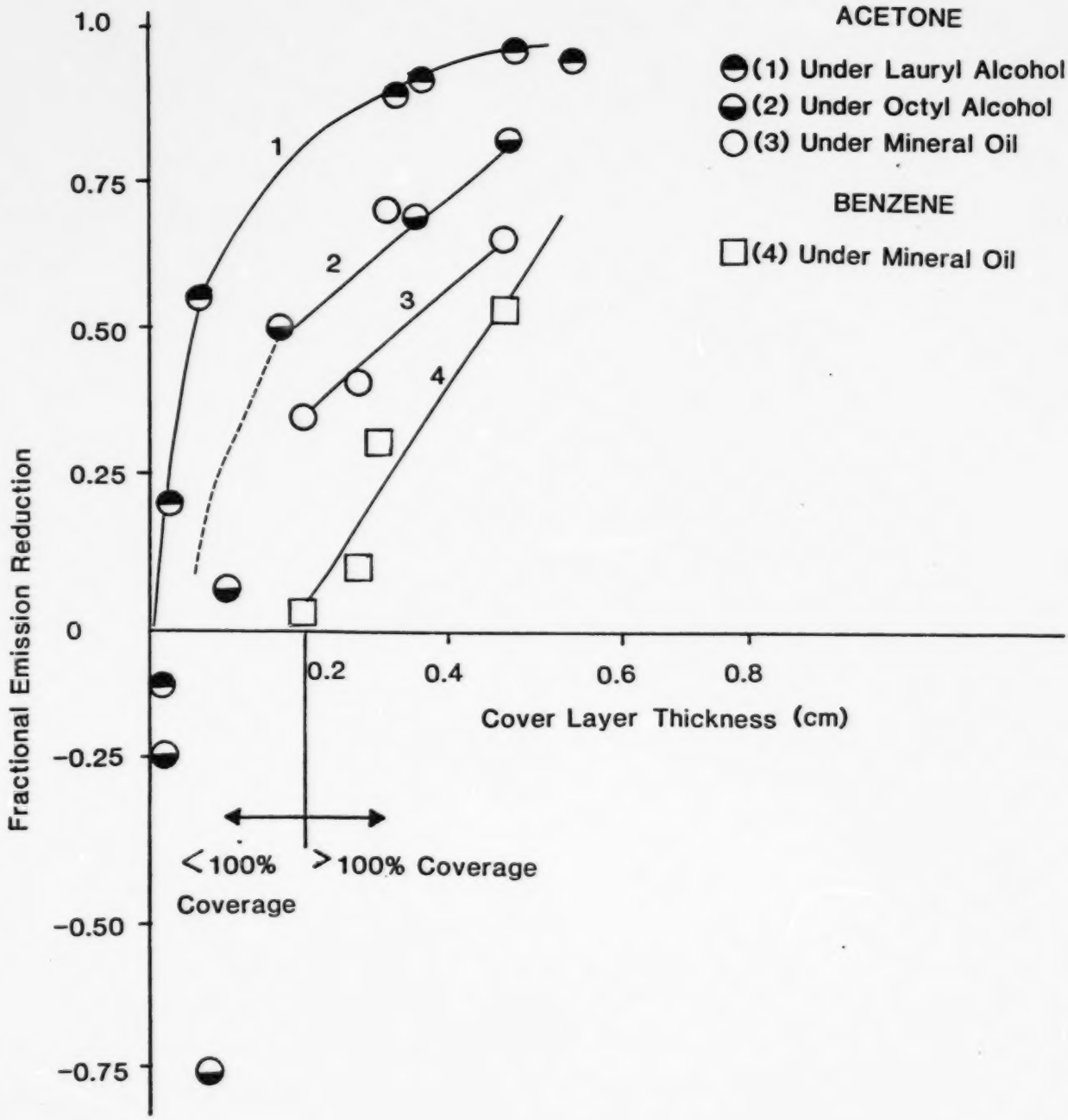


Figure 7-8: Fractional Emission Reduction versus Cover Thickness

It can be noticed from Table 7-3 that certain emission reductions are reported as negative. These instances reflect emission enhancements that were observed in some situations when the water surface was not completely covered by the immiscible organic liquid. The appearance of the surface during these instances with partial coverages showed the organic layer collecting in pools, or lenses, on the water surface. Further, those lenses were in constant motion, rapidly changing shape as well as location. The motion was much more in evidence with octanol than with lauryl alcohol. It seems apparent that the near surface mixing brought about by the motions of the lenses caused a significant increase in mass transfer from the water to the air. We also observed that this effect is much less obvious for the lauryl alcohol cover. This is suggested to be due to high solubility of octyl alcohol in water 586 mg/l at 25°C, (Seidell (1941)) as compared to that of lauryl alcohol in water 2mg/l at 25°C, (Kinoshita, et. al., (1958)). Due to the high solubility of octanol, the eddies which bring fresh material to the surface from the bulk liquid destablizes the interface causing "interfacial turbulence" whereas lauryl alcohol which forms a stronger monomolecular film resists such destablizing effects. These interfacial movements are a result of the fact that the surface tension of a partially oil covered surface is quite sensitive to the convection currents on the surface arising from temperature gradients between the bulk water and air phases. This effect has been extensively investigated earlier by Himmelblau and Burnett (1970) in the absorption of ammonia into water. They reported that insoluble surface films (eg. lauryl alcohol) reduced the mass transfer whereas soluble surface films (eg. octanol) caused enhancement in mass transfer and also observed interfacial movements caused by the so-called Marangoni effects (Berg, 1972) whenever enhanced mass transfer was observed. Such effects are more significant when soluble surfactants (particularly ionic surfactants like dodecyl sulfate) are used. These effects are reviewed in more detail in Section 7-3 on ionic surfactants.

From the results enumerated above (Figures 7-3 to 7-8 and Tables 7-2 to 7-3) we make the following tentative conclusions:

(a) VOCs of low solubility (low π) seem to be retained better than compounds of high solubility (high π). Compounds of high solubility in the cover material seem to pass through the cover easily.

(b) The thicker the oil cover, the better reduction in VOC emissions was found to be.

(c) Under no-wind conditions when temperature gradients between the water and air phases become the dominating mechanism for VOC emissions, a complete cover of oil is essential for a reduction in VOC emission, this being especially so if the cover material has considerable solubility in water.

(d) A reliable predictive model is not available because of the non-availability of data regarding liquid phase mass transfer coefficients for volatilization of VOCs from a non-aqueous phase such as mineral oil.

7.2 Oil Cover - Windy Conditions

The behavior of an oil cover may be quite different when a wind blows across a covered impoundment. Particularly, unless the wind is very low, or the cover

quite thick, the oil may be blown aside, exposing considerable water surface (Springer, et al., 1983).

It is presumed that the VOC will be emitted, under conditions of partial coverage, by parallel path processes, more-or-less as shown in Figure 7-9. The VOC will distribute between the phases in accordance with the relative solubility, that is, the partition coefficient, π, which was seen to be an important parameter in the no-wind situation. Since there were no published experience with VOC emissions from a partially covered impoundment in the presence of wind, a laboratory investigation was undertaken.

A wind-tunnel, 4 ft (1.22m) wide by 3 ft (0.93 m) high by 24 ft (7.3 m) long was used as a simulator. This wind-tunnel was different from that described in the previous section. Clear acrylic windows were provided for viewing the interior of the wind-tunnel. A water "tank", 16 ft (4.88 m) long by 2 in. (0.05 m) deep was placed in the bottom of the wind-tunnel, across the entire width of the wind-tunnel. The wind-tunnel and blower was as described by Lunney (1983) and by Lunney, et al., (1984). A diagram of the apparatus is shown in Figure 7-10. A float-controlled, solenoid-operated valve was used to maintain a constant water level in the simulator. In order that the float not be subjected to wind and wave action, it was located in a small water box outside the wind-tunnel. The water box with the float was hydraulically connected to the water tank, and could be independently raised or lowered. Thus, it was possible to maintain any constant water level desired.

The wind velocity could be controlled by a damper located at the inlet of the blower (which was the outlet of the wind-tunnel), and the wind velocity could be measured upstream of the water-tank by a hot-wire anemometer which could be inserted through a hole in the bottom of the wind-tunnel.

In operation, one or more example VOC's were mixed with water in the tank, along with a quantity of mineral oil (similar to the mineral oil used in the no-wind simulator). The blower was started and concentrations of chemical in the tank were measured with time, until 80 to 90% of the VOC had evaporated.

Two wind speeds were used, a high and a low. The high wind speed was approximately 7.9 m/s, and the low speed was approximately 4 m/s, as measured 2 inches (0.05 m) above the bottom of the wind-tunnel. The wind speeds were measured in each case, but there were small variations from run-to-run.

The chemicals (VOC) used in this study were benzene, toluene, methylene chloride and ethyl ether. All of these chemicals volatilize from water solution under liquid-phase control because of high Henry's law constants, and thus behave similarly to most hazardous VOC of interest.

The mineral oil was a "medium" grade. The measured viscosity was 52± 0.5 cP at 25·C and the measured density was 0.8± 0.05 g/cm^3 also at 25·C.

The experimentally measured partition coefficients were:

Benzene, π = 130
Toluene, π = 102
Methylene Chloride, π = 13
Ether, π = 5

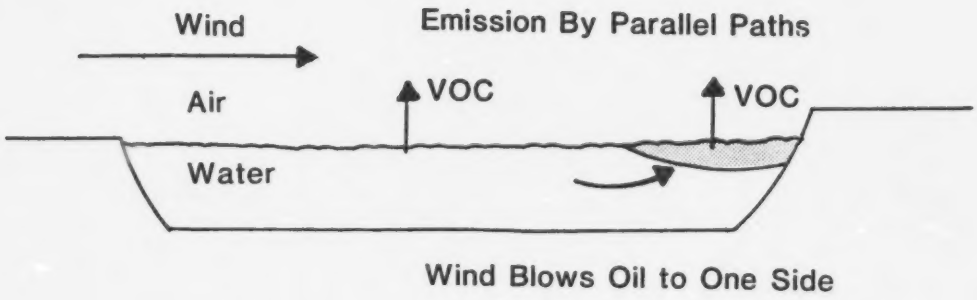


Figure 7-9: Oil Layer on an Impoundment Surface Under the Influence of Wind

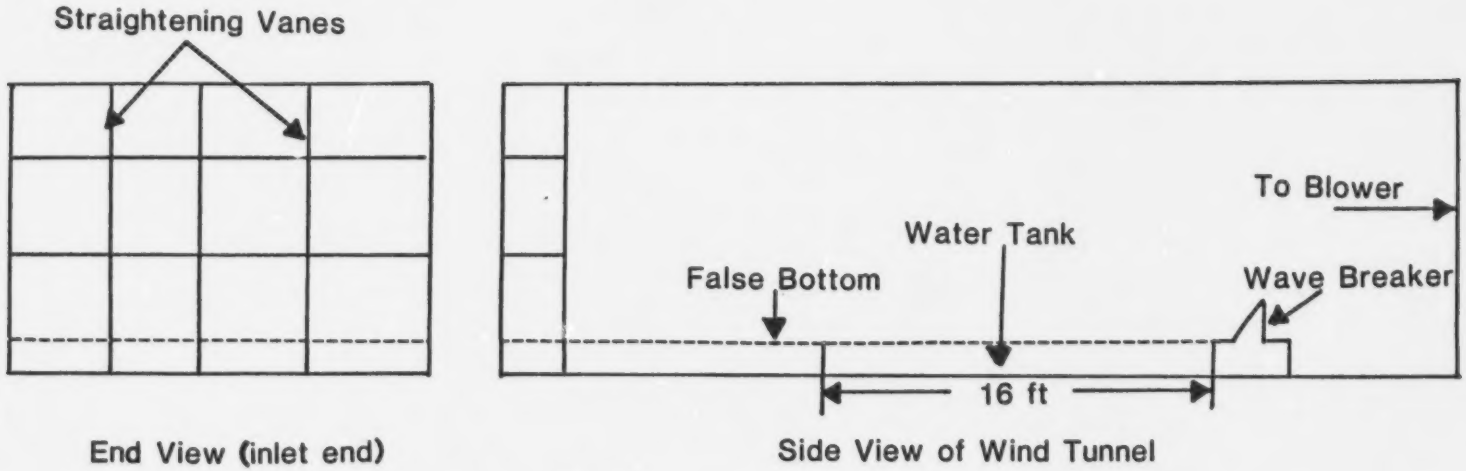


Figure 7-10: Wind Tunnel Arrangement

The results were analyzed by a parallel path, competitive phase model which was based on the assumption of equilibrium between the water and oil due to wind-induced mixing. Since the oil was observed to form a "slick" at the down-wind end of the water tank, the total emission rate, E, is given by a summation of the rates from each phase surface.

$$E = K_w s_w \Delta C_w + K_o s_o \Delta C_o \qquad (7\text{-}8)$$

where the subscript w refers to the water phase and the subscript o refers to the oil phase, and

K = overall liquid phase mass transfer coefficient, m/s
s = exposed surface area of respective phase, m^2
ΔC = concentration driving force for the respective phase kg/m^3 (with the air phase concentration negligibly small, $\Delta C \cong C$).

As stated earlier, we assume K_w is essentially liquid phase controlled, that is, the resistance in the adjacent air phase is negligible, so that $K_w \cong k_w$, where k_w is the individual liquid phase mass transfer coefficient.

The oil phase behavior, however, may not be entirely liquid phase controlled, so we formulate a traditional two-resistance equation:

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{1}{\theta k_g} \qquad (7\text{-}9)$$

where k_o = individual liquid phase coefficient, m/s
k_g = individual gas phase coefficient, m/s
θ = equilibrium constant between oil and air, analagous to Henry's law constant, dimensionless.

We note, from characteristics of equilibria, that

$$\theta = H/\pi, \text{ and } C_o = \pi C_w$$

where H = Henry's law constant for water/air equilibrium, and
π = partition coefficient between oil and water, dimensionless.

The combined rate of removal of chemical from both phases is then, if we consider the concentration of chemical in air to be negligibly small,

$$E = k_w s_w C_w + \frac{1}{\frac{1}{k_o} + \frac{\pi}{H k_g}} s_o \pi C_w \qquad (7\text{-}10)$$

In order to evaluate the process as a control method, the fractional reduction, R is defined

$$\text{Fractional Reduction, } R = \frac{E' - E}{E'} = 1 - \frac{E}{E'} \qquad (7\text{-}11)$$

where E' = emission rate without oil, kg/s
E = emission rate with oil, kg/s.

Without oil, the equivalent uniform VOC concentration would be:

$$C' = \frac{\text{total VOC}}{\text{total volume}} = \frac{C_w V_w + C_o V_o}{V_w + V_o} \qquad (7\text{-}12)$$

but since $C_o = \pi C_w$, this becomes

$$C' = \frac{C_w(V_w + \pi V_o)}{V_w + V_o} \qquad (7\text{-}13)$$

Then, the control-free emission rate is

$$E' = \frac{C_w(V_w + \pi V_o)}{V_w + V_o} \; k_w(s_w + s_o) \qquad (7\text{-}14)$$

Combining the equilibrium relations and Eq. (7-8), the controlled emission rate is

$$E = (k_w s_w + K_o s_o \pi) C_w \qquad (7\text{-}15)$$

then

$$R = 1 - \left[\frac{k_w s_w + K_o s_o \pi}{V_w + \pi V_o}\right] \frac{d}{k_w} \qquad (7\text{-}16)$$

where d = depth of the impoundment, m.

It can be shown that the greater the value of the partition coefficient, π the more effective is this method as an emission control technique. Primarily, this is because the coefficient for transfer from the oil, K_o, is smaller than K_w, and an increased solubility of the volatile in the oil will decrease the value of K_o, as well as decrease the VOC concentration in the water phase where there will be a higher coefficient. It is noted that an increasing value for the partition coefficient has the opposite effect for the three-resistance model presented earlier for the no-wind condition.

From a practical point, it is probable that K_o is the least well known of the parameters in all the foregoing, although it is possible to estimate a value from mass transfer considerations. No studies have ever been done which might specifically shed light upon the mass transfer from confined oil slicks.

We assumed a mixing mechanism similar to wind induced mixing of a water body, then attempted to assess the effect of physical properties thereon. For the water alone, we assumed a mass transfer relation in the form of

$$Sh = a\, Re^{.8}\, Sc^{1/3} \qquad (7\text{-}17)$$

where Sh = Sherwood No., dimensionless
(Sh = k L/D)

k = mass transfer coefficient, m/s

L = characteristic length, m

D = diffusivity, m^2/s

Re = Reynolds No., dimensionless
(Re = L v/ν)

v = phase velocity, m/s (this is the velocity induced in the liquid by the wind)

ν = kinematic viscosity, m^2/s

Sc = Schmitt No., dimensionless
(Sc = ν/D)

a = a proportionality constant

Next, we assume the form of the relation is the same for the oil slick or for the water, and that the parameters of phase velocity and characteristic length are the same. Comparing the mass transfer coefficients for the oil and water then gives:

$$\frac{k_o}{k_w} = \left(\frac{\nu_o}{\nu_w}\right)^{-0.47} \left(\frac{D_o}{D_w}\right)^{2/3} \qquad (7\text{-}18)$$

where D_o and D_w are the diffusivities of the VOC in oil and water, respectively.

The oil phase diffusivity can be compared to the water phase diffusivity by the Wilke-Chang method (Treybal, 1980). Thus, we arrive at a final estimate for the oil phase coefficient as

$$k_o \cong 0.04\ k_w \qquad (7\text{-}19)$$

The value of k_g for use in Eq. (7-9) was assumed to be according to McKay and Matsugo (1973).

Even though there are some unproved premises in the estimate of the oil phase coefficient, K_o, it is apparent that the value will not likely be more than 5% of the equivalent value for water, K_w.

The results of experimental efforts to confirm the parallel path, competitive phase model are shown in Table 7-4. An interesting conclusion is that the method generally appears to be more effective at higher winds for chemicals with a high partition coefficient, but the opposite is true for the chemicals with lower partition coefficients. The predictive model is not quite conclusive.

Oxygen Reaeration

Since oxygen reaeration rates were of concern, a series of experiments were prepared to measure the effects of the oil layer on the oxygen uptake. The work was done by measuring the effective mass transfer coefficient for oxygen with

Table 7-4. Results of wind-tunnel tests on a partial coverage oil layer

Chemicals	Wind Speed (m/s @ 2")	Volume[1] of oil (m^3)	No. of Trials	Fractional Reduction (R. as defined in text) (Exptl.)	(Model)	s.d.[2] (%)
Benzene	4.1	0.0026	3	0.30	0.35	15
Toluene	4.15	0.0026	3	0.37	0.40	15
	7.62	0.0026	2	0.11	0.50	34
Ether	3.98	0.0026	2	-0.17[3]	0.27	2.8
	7.91	0.0026	1	0.14	0.12	--
Methylene Chloride	4.05	0.0026	2	0.66	0.17	23
Benzene	3.51	0.013	3	0.43	0.82	36
	7.93	0.013	3	0.84	0.84	46
Toluene	3.51	0.013	3	0.37	0.81	36
	7.93	0.013	3	0.76	0.84	33
Ether	3.51	0.013	3	0.64	0.37	52
	7.93	0.013	3	0.73	0.27	42
Methylene Chloride	3.51	0.013	3	0.01[3]	0.46	18
	7.93	0.013	3	0.82	0.39	27

1. 0.0026 m^3 oil was approximately 1% by mass of the simulator tank volume while 0.013 m^3 was about 5% oil by mass.
2. Standard deviation for the experimental values expressed as a percentage of the mean experimental value.
3. These results appear to be anomalous and without apparent explanation.

and without oil at the two wind speeds used for volatilization. It was found that, generally, within the limits of experimental error that the oxygen reaeration rate was retarded in proportion to the fraction of the surface covered by oil. This observation is in keeping with the premise that a small oil coverage of the surface does not materially affect the turbulence and mixing in the water, and further, that oxygen interaction with the oil is negligible.

Nature of the Oil Slick

The oil was observed to quickly move to the down wind end of the water tank and to stay there, occupying approximately a constant area. Efforts were made to model this behavior to determine a means of predicting the surface area which would be occupied by the oil layer for a given situation.

It was assumed that the oil would be pushed into a wedge-shaped pool similar to that shown in Figure 7-11. In Figure 7-11, the dashed line represents the nominal water level. From hydrostatic principles we predict a relation between the distances Z and Z' as follows:

$$Z\rho_o = Z' (\Delta\rho) \qquad (7\text{-}20)$$

where ρ_o = oil density, kg/m^3
$\Delta\rho = \rho_w - \rho_o$
ρ_w = water density, kg/m^3

A similar relationship exists between h and h' which represent the oil layer depths at the end of the water tank (or on the berm of an impoundment). The force balance diagram in 7-10 shows the relationship between F_w and F_ρ where F_w is the drag force due to the wind and F_ρ is the force due to the weight of the oil.

$$F_\rho = \frac{1}{2} g\rho_o \, b \, h \qquad (7\text{-}21)$$

where g = acceleration of gravity, 9.8 m/s^2
The drag force of the wind on the oil can be expressed as (from Levich, 1962)

$$F_w = \frac{1}{2} C_D \, U^2 \, \rho \, b \, L \qquad (7\text{-}22)$$

where C_D = drag coefficient, dimensionless
U = wind velocity, m/s
ρ = air density kg/m^3

Further, the drag coefficient can be estimated by (Levich, 1962)

$$C_D = 0.074 \, Re^{-0.2} \qquad (7\text{-}23)$$

where Re = Reynolds No. dimensionless
($R_e = U L/\nu$)
= kinematic viscosity of the air, m^2/s

Thus:

$$F_w = 0.037 U^{1.8} L^{1.8} \rho b / \nu^{0.2} \qquad (7\text{-}24)$$

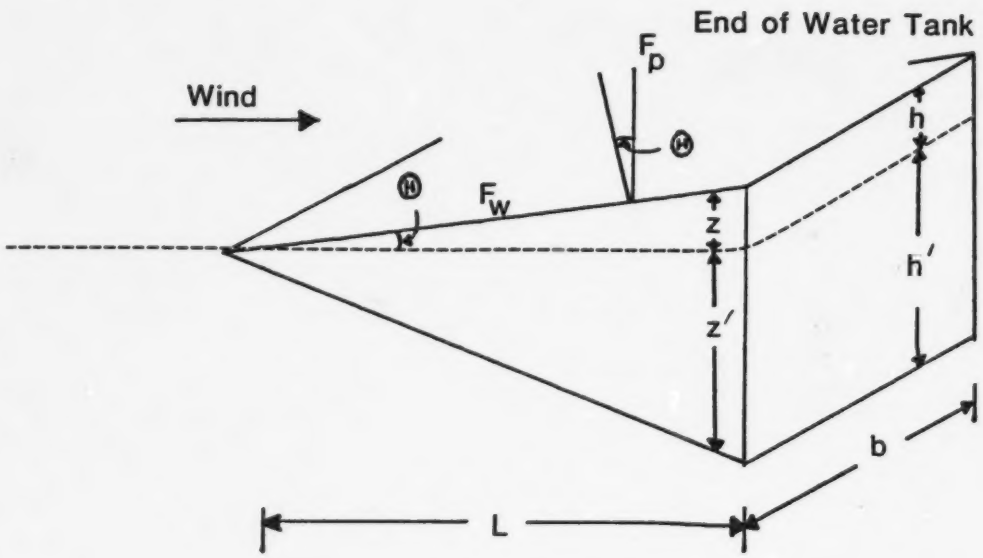


Figure 7-11: Wedge-Shaped Oil Slick Model

$$L^{2.4} = \frac{V_o \sqrt{\rho_o/\rho_a}}{\frac{1}{2} L\, b(1+\rho_o/\Delta\rho) x .087\, U^{0.9}\, \nu_a^{0.1}} \qquad (7\text{-}33)$$

$$L = \left[\frac{V_o \sqrt{\rho_o/\rho_a}}{.043\, b\, (1+\rho_o/\Delta\rho)\, U^{0.9}\, \nu_a^{0.1}} \right]^{\frac{1}{2.4}} \qquad (7\text{-}34)$$

This expression can be used to estimate the area of a surface impoundment covered by an oil slick provided the wind velocity is known.

In order to check the suitability of Eqn (7-34) to predict the size of the resulting oil slick under windy conditions, a series of experiments with dyed oil were performed.

Observation holes were cut in the sides and top of the wind-tunnel and Plexiglas windows were installed. A quantity of the oil was dyed with Sudan III red dye. Oil was added in predetermined amounts and the blower was started to create the desired air velocity.

The size of the resulting oil slick was estimated by visual observation.

The results of the experiments are shown in Table 7.5.

Table 7-5. Results of Oil Slick Observation Experiments

Wind Speed (m/s)	Oil Volume (m^3)	Length of Oil Slick (m)	
		Observed	Model
3.76	0.0005	0.65	0.35
7.87	0.0005	0.15	0.26
3.8	0.001	0.69	0.46
3.8	0.0002	0.75	0.61
4.06	0.003	0.78	0.71
7.87	0.003	0.30	0.55
2.28	0.003	0.32	0.88
5.60	0.003	0.38	0.63

Of the eight determinations, the model predicts lower values for the length in five (5) cases and higher values in three (3) cases. Those where the model underpredicts are all lower wind speeds, and where the model predicts higher values, are all higher wind speeds. It is suggested that two aspects of the model are perhaps incorrect. The first is that the movement of the water under the oil will exert more than just static pressure and the underside of the oil slick, hence, an additional force would be required in the force balance to compensate. The second problem is with the simplified drag coefficient. The expression used probably won't suffice for all wind speeds, and the drag is no doubt effected by the presence of the water surface as well. A great deal of experimentation would be required to resolve these problems.

It is now noted that the angle θ can be expressed as

$\theta = \arctan (F_w/F_\rho)$

$$\text{hence, } \tan\theta = \frac{.037\, U^{1.8} L^{1.8} \rho_a \nu_a^{0.2}}{\frac{1}{2}\, g\, \rho_o\, h} \tag{7-25}$$

$$\tan\theta = \frac{h}{L} \tag{7-26}$$

$$\text{thus: } h = \frac{.037 U^{1.8} L^{1.8} \rho_a \nu_a^{0.2}}{\frac{1}{2}\, g\rho_o\, h} \tag{7-27}$$

$$\text{and } h^2 = \frac{.037 U^{1.8} L^{2.8} \rho_a \nu_a^{0.2}}{\frac{1}{2}\, g\rho_o} \tag{7-28}$$

But

$$V_o = \frac{1}{2} L\, b\, (h+H') = \frac{1}{2} L\, b\, h\, (1 + \rho_o/\Delta\rho) \tag{7-29}$$

where V_o = volume of oil, m^3

Solving for h:

$$h = \frac{V_o}{\frac{1}{2} L\, b\, (1 + \rho_o/\Delta\rho)} \tag{7-30}$$

$$\text{and } h = \left(\frac{.037 U^{1.8} L^{2.8} \rho_a \nu_a^{0.2}}{\frac{1}{2}\, g\rho_o}\right)^{1/2} = 0.087\, U^{0.9} L^{1.4}\, \nu_a^{0.1} \left(\frac{\rho_a}{\rho_o}\right)^{1/2} \tag{7-31}$$

Eliminating h:

$$\frac{V_o}{\frac{1}{2} L\, b(1+\rho_o/\Delta\rho)} = 0.087\, U^{0.9} L^{1.4}\, \nu_a^{0.1} \left(\frac{\rho_a}{\rho_o}\right)^{1/2} \tag{7-32}$$

Solving for L:

In applying the slick behavior model to an actual impoundment, the depth of the impoundment would have some effect. Probably the effect would be relatively small, since it would not effect the surface drag, but might effect the pressure exerted by the water and that body of oil below the water-line.

In conclusion, an oil layer on the impoundment surface will reduce VOC emissions for a given quantity of VOC in an impoundment. The reduction in emissions is greater than that which could be accounted for by the water area reduction alone, although this will prove to be true only if the VOC is more soluble in the oil than in the water.

An approximation of the quantity of oil required for a specified slick size in a given wind can be obtained through the use of Eqn (7-34).

7.3 Use of Surfactants as a Control Option

Here we briefly review the use of surfactants to control mass transfer of materials across the water-air interphase. Maintenance costs of surfactant covers have been suggested to be relatively low, but the effectiveness of surfactant monolayers in surface impoundments are questionable (Vogel, G.A., 1985). Surfactants (especially, long chain alcohols like hexadecanol) have been traditionally used to control water evaporation from reservoirs and lakes; it has to be remembered that water evaporation is a gas phase controlled process while most of the VOC emissions are liquid phase controlled.

Even though the use of surfactants did not form part of this project, we felt it desirable to enumerate here the various theories, mechanisms and experiments we uncovered as part of the general review on VOC emission controls.

7.3-A No-wind, stagnant conditions:

Surfactants have the tendency to concentrate at an interface and therefore modify the structure and properties of the interface. If a molecule crosses the interface, (See Figure 7-12) it encounters a total resistance R_T composed of three separate diffusional resistances, due respectively to diffusion in the liquid phase, across the monomolecular region constituting the interface and through the gas phase, i.e.,

$$R_T = R_\ell + R_i + R_g \qquad (7\text{-}35)$$

Of the three resistances, R_ℓ is usually the predominant one. This corresponds to molecular diffusion through a quiet unstirred micro region adjacent to the surface. Interesting cases do exist whereby R can be made so low as to make R_i or R_g controlling. Davies and Rideal (1963) derived an equation for R_i based on kinetic theory of gases as

$$k_i = \frac{1}{R_i} = \alpha \left[\frac{RT}{2\pi M} \right]^{1/2} \qquad (7\text{-}36)$$

Where k_i is the transfer coefficient across the surfactant phase, α is the accomodation coefficient or the fraction of molecules of the chemical striking the surface that condense on the surface, R is the gas constant in ergs./mol/K and M is the molecular weight. If we then attribute a three phase resistance

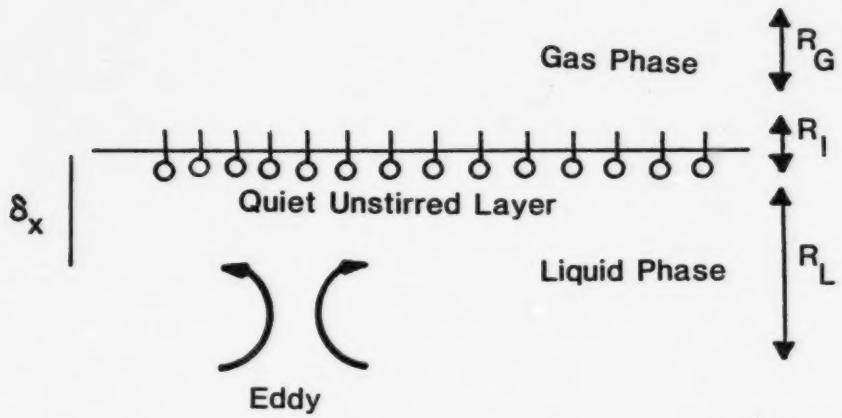


Figure 7-12: Various Phase Resistances Encountered by a VOC During Desorption in a Solution Containing a Long Chain Surfactant (Represented in the Diagram by the Symbol —o)

model for the whole process we can obtain for the overall volumetric mass transfer coefficient,

$$K = \frac{1}{h}\left[\frac{1}{k_\ell} + \frac{RT}{H_c\, k_i} + \frac{RT}{H_c\, k_g}\right]^{-1} \qquad (7\text{-}37)$$

where H_c is the Henry's constant for the chemical, h is the depth of the impoundment, k_ℓ and k_g represent the liquid and gas phase mass transfer coefficients respectively. The equation for k_ℓ also suggests that there may be an activation energy barrier for transport of chemicals across the surfactant phase. This effect is most marked in the retardation of water evaporation (which is gas phase controlled) by monolayers of long chain alcohols. Approximate calculations also show that R_i is very small compared to R_ℓ and hence for liquid phase controlled chemicals, the surfactant phase exerts its influence by increasing the viscosity of the microregion near the surface and thereby increasing R_ℓ. According to the classical two film theory this amounts to decreasing the diffusion constant (D_ℓ) of the chemical in the boundary layer or increasing the thickness of the boundary layer. To use the penetration or surface renewal theories one can say that either the diffusion constant (D_ℓ) or the residence time of a packet at the surface are reduced. Goodridge and Robb (1965) suggest that these two interfacial effects (viz. energy barrier and hydrodynamic effects) are inseparable and may both be operative simultaneously.

The effects of the so called "soft-ice" near the surfactant phase has been further explored by McCoy (1982) and Yousef and McCoy (1983). They carried out theoretical modeling of the effects arising from the presence of an oriented water layer next to the ionic head groups of the surfactant molecules oriented at the aqueous-air interface. They also suggest that the capacity of the monolayer to retain water molecules should not be ignored. Their idea of a rigid structured water layer next to the surfactant was derived mainly from the work of Drost-Hansen (1977) who suggested that the thickness of such a vicinal water layer could be as large as 10^3 A°. The same arguments have been proposed and proven quite convincingly by Hansen (1961) and Bilkaldi *et al.*, (1980). The overall results of McCoy's (1983) work is that D_s (diffusion constant in the interface region) is orders of magnitude less than D_ℓ in bulk liquid. If this hydrodynamic effect is that considerable, one should observe quite marked effects on the volatilization of certain chemicals of environmental significance, most of which are liquid-phase controlled.

7.3-B No-wind, stirred condition:

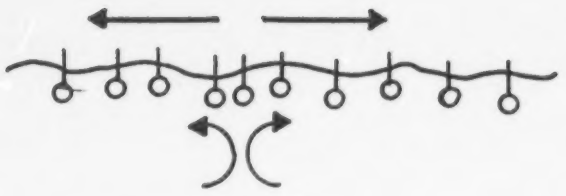
When the liquid side of the solution is stirred, it has been suggested (Lewis and Whitman, (1924)) that the liquid surface remains stagnant up to a distance δ_x from the interface, this being dependent on the rate of stirring. This so called "laminar sublayer" then decides the value of R_ℓ. On the other hand when steady state conditions do not exist (as is possible in most realistic surface impoundments) the laminar sublayer cannot be a deciding factor; the mean velocity of the liquid then controls the value of R_ℓ. We then have to use either the penetration theory or surface renewal theories to calculate R_ℓ.

Even under stirred conditions, the presence of surfactants can indeed influence the value of R_ℓ markedly by either suppressing or enhancing the bulk phase eddies. Let us analyze this situation in detail.

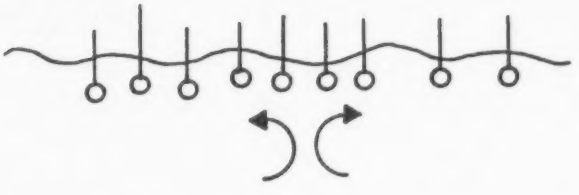
The interfacial tension (surface tension in the case of liquid/air interfaces) is a sensitive function of both temperature and surfactant concentration at the interface (Adamson 1982). These effects give rise to what is called "interfacial turbulence" (Berg, 1972). Two related effects arising out of this phenomena which have been studied extensively are the Pearson problem and the Sternling-Scriven problem (Berg, 1972, Sternling and Scriven, 1959). Let us consider systems which are dilute solutions of moderately to strongly adsorbed solutes. It can be realized that the case of insoluble monolayers will then be a limiting case. The same arguments will also apply to the case of floating immiscible organic liquids on the aqueous surface when the surface is only partly covered, and the organic liquids happen to be alcohols (long-chain) and not hydrocarbons. Whether or not the surfactants by themselves are transferring across the interface, their presence may exert an enormous influence on the system against interfacial turbulence and stress flows.

Following is a qualitative discussion of these effects caused by the presence of strongly adsorbed solutes. Consider a layer of adsorbed solute at a liquid-gas interface (See figure 7-13), and imagine an eddy in the bulk phase (this can result from both temperature as well as density gradients) attempting to dilate the surface. The eddy will sweep away adsorbed solute from the dilated spot, tending to clear it. This will by itself reduce the surface concentration, which in turn effects the surface tension giving rise to a surface flow of the material tending to make the interface "snap-shut". Under such circumstances since surface concentration (mol/cm^2) is large, even if the eddy from the interior is richer in solute than the bulk liquid present below the surface, it still contains solute in insufficient quantity to rapidly restore the locally reduced Γ. In the limit, as the "solute" becomes a spread monolayer (this happens for very long chain alcohols) the bulk eddy would provide no help at all in restoring the surface concentration. The surface is then left to its own devices to restore uniformity in, and its chief tool in this respect is "surface-flow" driven by surface tension gradients. The magnitude of the stablizing influence then depends, among other things, on the rapidity with which non-uniformities in Γ can be eliminated. If the realtive adsorption is low (but positive) and the concentration gradient is such that the bulk is richer than the sublayer, we actually have a destablizing effect. This will be the case when the cover material is of considerable solubility in the water. Let us consider a series of situations where the cover material forms monolayers, each with increasing chain length (egs. octanol, lauryl alcohol, hexadecanol). The eddies which bring material to the surface from bulk liquid are shown in the figures.

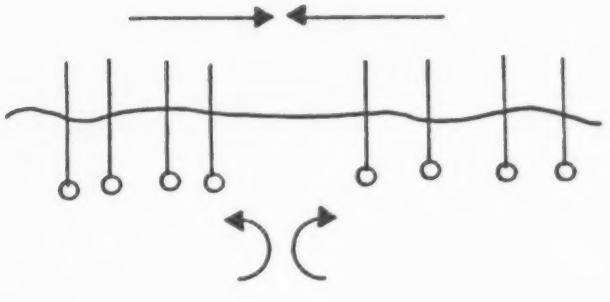
Class A molecules are those that are extremely soluble in water so that the micro region below the surfactant phase is rich in solute as compared to the surface (egs. most of the short chain alcohols). Octanol which has a solubility of 500 mg/l also falls in this class. The other extreme case is Class C where the surfactants are insoluble in water (egs. lauryl alcohol of solubility 2 mg/l at 25°C and alcohols of higher than 12-carbon chain). In such cases the eddy is of no consequence since the surface provides a large Γ and a high back pressure which prevents interfacial instability from being set up. Hence, in such cases a monolayer would by itself retard the movement of chemicals across the interface. One has to consider the fact that longer chain surfactants provide more stable monolayers and if present at sufficiently high concentrations can lead to the formation of the so-called "solid films" (Adamson, 1982) which by itself



(A) CLASS I (SMALL Γ). EDDY CAUSES "OVERHEALING" AND GENERATES INSTABILITY. LIQUID RICH IN "SOLUTE" RELATIVE TO THE NEEDS OF THE SURFACE.



(B) CLASS II (MODERATE Γ). EDDY JUST ABLE TO HEAL SURFACE, NO EFFECT ON DISTURBANCES. LIUQID "MODERATELY RICH" IN SOLUTE RELATIVE TO THE SURFACE.



(C) CLASS III (LARGE Γ). EDDY LITTLE OR NO HELP IN RESTORING UNIFORM CONCENTRATION. LIQUID "WEAK" IN SOLUTE REALTIVE TO THE NEEDS OF THE SURFACE.

Figure 7-13: Bulk Eddy Disturbance for Solutions Containing Surfactants of Increasing Number of Carbon Atoms in the Long Chain

provide for the formation of the so-called "soft ice" described earlier and thus effect the value of k_ℓ.

Most of the experimental results available so far for dynamic situations where stirring induces lowering of R_ℓ are based on gas absorption into aqueous columns and transfer of material between two liquid phases, in contact. For clean surfaces J. B. Lewis (1954) proposed the following equation

$$k_1 = 1.13 \times 10^{-7} \quad \nu_1 \left[Re_1 + \frac{Re_2 \, \eta_2}{\eta_1} \right]^{1.65} + 0.0167 \quad \nu_1$$

for mass transfer of a solute between oil and water phases in contact (for stirred systems) where subscripts 1 and 2 refer to the two liquid phases, η denotes the viscosity, ν the kinematic viscosity (η/ρ), Re denotes the Reynold's number of either phase $L_2N/$, L being the tip to tip length of the stirrer blades and N the number of revolutions of the stirrer per second. By interchanging the subscript k_2 can also be obtained.

Though numerical agreement of ±40% has been achieved in many cases, a frequent criticism of the above equation is its lack of dependency on the diffusion constant of the solute in either phase. This was overcome by Davis and Myers (1961) in their empirical correlation

$$k_1 = 0.00316 \left(\frac{D_1}{L} \right) (Re_1 \, Re_2)^{0.5} \left(\frac{\eta_2}{\eta_1} \right)^{1.9} \left(0.6 + \frac{\eta_2}{\eta_1} \right)^{-2.4} \left(Sc_1 \right)^{5/6}$$

where D_1 is the diffusion constant of the solute in phase 1 and Sc_1 is the Schmidt number for phase 1 (ν_1/D_1).

Lewis (1954) proposed the following equation for transfer in the presence of a monolayer of surfactant (eg. protein) at the interface where the value of k_1 is reduced by as much as 80%:

$$k_1 = 1.13 \times 10^{-7} \quad \nu_1 \, Re_1 \, 1.65 + 0.0167 \, \nu_1$$

Notice that this equation has no dependence on Re_2; physically this means that the stirring in the oil side of the interface has no effect because the turbulent eddies of oil have their momentum damped out at the interface by the surfactant.

The overall conclusion then is that the presence of a long chain surfactant or long chain alcohol) of very low aqueous solubility would considerably reduce mass transfer of volatile solutes between air/liquid or liquid/liquid interfaces, both of which are of importance environmentally.

The influence of stirring in the aqueous phase upon mass transfer of benzene to air phase has been studied by Smith et al., (1980). Their results showed a reduction of more than 50% in k value even at stirring speeds of 270 revolutions/minute (the surfactant they used was 0.003% Triton X-100). Their results show conclusively that surfactants are indeed effective in reducing VOC missions even under vigorously stirred conditions. A combination of pilot-plant scale work and laboratory scale investigations would help in obtaining mass transfer correlations for VOC emission predictions in the presence of surfactants.

7.3-C No-wind condition, warm water-cold air scenario:

A scenario of warm water in contact with cold air can arise in several situations involving hazardous wastes. Examples are holding and receiving ponds which contain warm water contaminated with hazardous VOCs, towards the end of the day when the sun no longer keeps the air warm, the natural convection mechanism has been shown to be the predominant mechanism of VOC emission (Thibodeaux, 1981). The same situation can occur when lakes are cooling in the fall of the year. We have conducted extensive experiments on pilot-plant scale to study how VOC emission reduction under these conditions can be achieved by using floating immiscible organic liquid covers such as octanol, lauryl alcohol and mineral oil (Valsaraj et al., 1985 and Springer et al., 1985). We found that compounds of low oil solubility and high aqueous solubility were controlled very well when the surface was covered completely by even as much as 0.2 cm thick oil cover. On the other hand, if the surface coverage was partial (<5%) and the cover material (eq. octanol) had a considerable aqueous solubility (approx. 500 mg/l at 25°C) it gives rise to instabilities on the surface. The "lenses" of oil formed on the surface move erratically on the surface because of surface tension gradients between uncovered regions and "lenses" giving rise to "interfacial turbulence" which promotes mass transfer. However, when the aqueous solubility of the cover was reduced by the use of lauryl alcohol (solubility $\simeq$ 2 mg/l at 25°C) instead of octanol, such enhancements at low coverages disappeared. The explanation for these observations is similar to the ones we enumerated earlier for no-wind stirred conditions using surfactants of various chain lengths (see Section 7-2).

We hope that the study of the same phenomena using ionic surfactants and other alcohols commonly used in evaporation reduction in lakes, ponds and reservoirs (eg. Lissapol, hexadecanol, etc.) can provide us further information regarding the mechanism of such emission enhancements at very low surface coverages and reductions at high surface coverages. It must also be remembered that floating oil covers such as octanol introduce an additonal air emission problem (under the warm water-cool air condition), i.e., that of the volatilization of the cover itself (it also causes extensive odor problems) whereas the use of surfactants eliminates such problems because they are non-volatile.

7.3-D Wind-enhanced conditions:

The presence of surfactants on the surface under stagnant conditions do not affect the value of R_g at all. On the other hand when air is passed over a liquid surface covered by a monomolecular layer of surfactant (eg. hexadecanol, ref. McRitchie, 1969) the hydrodynamic conditions over the liquid surface are so modified as to retard the evaporation of water considerably. This effect is explained by Davies and Rideal (1961) as due to the following reason: The stress (τ) on the monolayer due to the moving air compresses the monolayer, producing a surface pressure gradient ($\frac{d\pi}{dx}$) which opposes the stress. The back stress of the monolayer reduces the net stress on the surface, and therefore consequently increases the size of the air side diffusion boundary layer. This may effect the evaporation of water more because it is completely gas phase controlled. Parker (1984) recently found that aerodynamic modifications of the boundary layer above a water surface can also significantly reduce the emission of ethyl ether (a liquid phase controlled chemical). One should, therefore, expect that similar effects should be observable in the case of surfactant monolayer covers

also. One argument which has been frequently used against the use of surfactants has been that under wind induced turbulent conditions the surfactant is blown towards one side thereby reducing their effectiveness (Ehrenfeld, Bass, Ong, 1984). Even in the presence of wind, surfactants (like hexadecanol) have been known to provide at least a monolayer coverage. Under these circumstances, such considerations as modifications of the air side diffusion boundary layers by surfactants and their effects on VOC emissions have not been given any attention at all. At least in surface impoundments where natural convection mechanism of VOC emissions predominate, it is felt that adequate investigations have to be carried out to test the effectiveness of surfactants. Of course, one should recognize the fact that the use of surfactants are restricted to anaerobic conditions due to the fact that some of the surfactants are biodegradable. Even so, today there are available several other surfactants which are non-biodegradable and the use of such surfactants may indeed be promising.

8.0 SYNTHETIC MEMBRANES OVER LANDFILLS

The use of synthetic membranes covering landfills is important from the standpoint of restricting water inflow, thus to the restricting of leachate accumulation. Probably, all hazardous waste landfills in the future will have synthetic liner materials covering them, somewhat in the manner suggested by Figure 8-1 which was proposed by Roulier (1982).

The flux of vapors through soils, either for landfill covers or otherwise has been the subject of several studies. At the present time, the mechanics of the transport process have not been adequately modeled. A comprehensive review of the state-of-the-art is presented by Springer, Valsaraj, Lunney and Thibodeaux (1985).

The flux of vapors through a landfill cap is treated by the series resistance concept, where each soil type encountered is a unique resistance. The expression for series resistance in this instance is

$$R_T = \sum_{i=1}^{n} L_i/D_{e,i} \qquad (8\text{-}1)$$

where R_T = total diffusive resistance, s/m
L_i = soil depth (for layer i), m
$D_{e,i}$ = effective diffusivity of the chemical in the soil, m^2/s

The estimate of the effective diffusivity of a vapor through the soil is based upon the work of Millington and Quirk (1961), which is

$$D_e = D\ (\varepsilon_l^{3.3}/\varepsilon^2) \qquad (8\text{-}2)$$

where D = Diffusivity of the chemical in air, m^2s
ε_l = soil gas filled porosity, dimensionless
ε = soil total porosity, dimensionless
The flux, then, is expressed as

$$N = (C^* - C)/R_T \qquad (8\text{-}3)$$

where C^* = the equilibrium concentration of VOC at the origin within the landfill, kg/m^3
C = air phase concentration above the soil, kg/m^3 (C is normally considered to be zero)
N = Flux of the vapor, kg/m^2s

Eqn (8-3) is appropriate for use when there is no convective flow of biologically generated gas. In the event there is a flow of bio-gas, the flux expression is somewhat more complicated. However, in the event of bio-gas flow, a synthetic membrane cover will be inappropriate because of the potential for the development of high internal gas pressures (Springer, Thibodeaux and Chathrathi, 1983). This same work, which was a computer simulation, showed that the flux would be enhanced somewhat (up to about 13%) by barometric pumping.

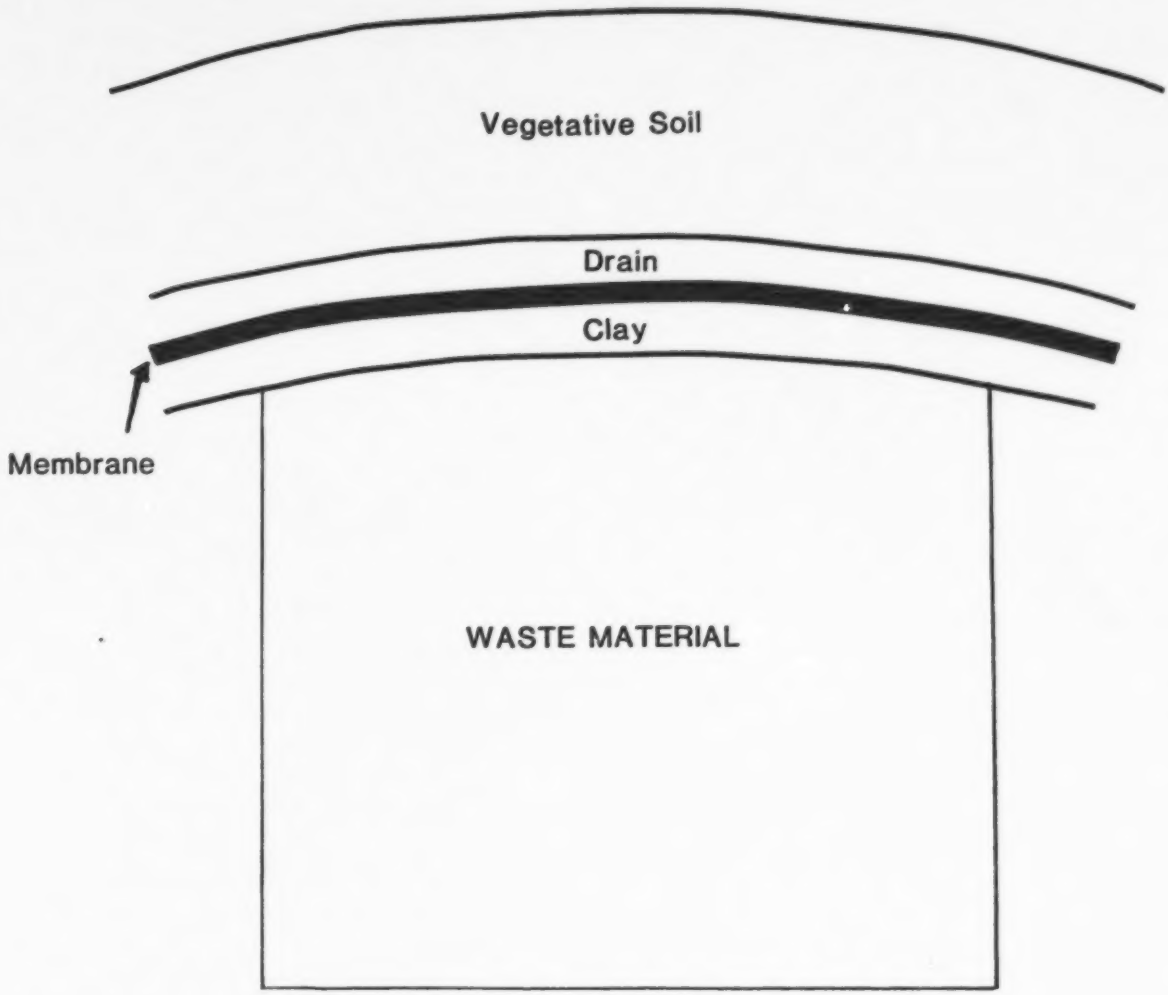


Figure 8-1: Proposed Landfill Cover Scheme Using Synthetic Membrane With Soil Layers

Unfortunately, the simplified mechanism of Eqn (8-3), even when adjusted for barometric pumping, does not adequately predict emission fluxes from landfills. Measured fluxes have exceeded the model by factors ranging from 1.5 to 25.

If a synthetic liner is to be placed over a landfill and adequately sealed to prevent lateral flow, then the liner resistance is included in the summation of equation (8-1). If the liner material is known to have a suitably low permeability, then it can be considered to be the controlling resistance or only resistance. However, it may often be found that the liner does not constitute the predominant controlling resistance, and in fact, may sometimes be a relatively minor part of the total resistance.

If the liner is the only significant resistance, then the flux expression is simply,

$$N = D_L (C^* - C)/L_L \qquad (8\text{-}4)$$

where D_L is the effective diffusivity of the chemical in the liner and L_L is the thickness of the liner.

In practice, there is not a large, public data base for liner permeability. In many instances manufacturers of the liner may have data available. In any specific instance it may be appropriate to measure the liner permeability directly for the VOC of interest. One such method is as outlined earlier in Section 3.0 of this report, and is reported in more detail below.

As a part of this project, we measured the apparent diffusivity of a number of organic chemicals in a sample of poly(vinylchloride)(PVC) film. In one part Surin (1982) measured the apparent diffusivities of 17 different chemicals through the film by a method similar to that outlined earlier.

In this measurement method, liquid samples of the chemicals were placed in small, wide-mouth, screw-cap glass jars of approximately 100 m capacity. The jars were small enough that they, with about 15-20 g of chemical sample could be weighed on a 200 g capacity balance. After the chemical was put into the jar, a piece of the PVC film was cut to fit the top opening, and then was clamped into place by a screw-on ring made by cutting a hole in a cap.

The jars of chemical, with PVC film and compression ring caps were weighed at predetermined time intervals in order to monitor the weight change. The jars were weighed several times a day.

The process was carried out at room temperature, which changed during each day, and from day-to-day. In order to moderate the temperature fluctuations, the jars were placed into holes cut in a Styrofoam block. Each jar was thus surrounded by a close fitting Styrofoam insulation, except at the top. One jar was selected as a temperature measurement sample, and had a thermocouple inserted through the PVC film and then sealed in place. Thus the temperature could be monitored with time. All the jars were considered to have the same temperature. The temperature outside the jar, between the jar and insulation was also monitored. The temperature ranged from 24·C to 32·C for the entire course of the experiment. During a typical day, the temperature would vary by about 3.5·C from low to high.

The flux was determined by the loss in weight versus the time. During the initial part of the experiment, the flux was not constant as the film was absorbing the chemical. In most instances, however, the flux became essentially constant (weight loss linear with time) after the initial period.

The diffusivity of the film was determined from the experimental data by an adaptation of equation (8-4). The flux, N, was determined from the constant rate weight loss and cover (film) area,

$$N = \frac{\Delta m}{\Delta t . A} \qquad (8\text{-}5)$$

where Δm = weight change, kg.
Δt = time difference, s
A = covering area, m^2

The vapor concentration within the jar was assumed to be that of saturation. Since the temperature changed somewhat with time, a time-weighted average determined from vapor pressure was determined from various values of vapor pressure at the various temperatures. The vapor pressures were interpolated from an Antoine equation for each chemical. The air-side concentration was assumed to be zero. Thus, the concentration driving force was simply the time-weighted average vapor pressures.

Finally, the apparent diffusivity was determined by

$$D_L = \frac{N}{\overline{C^*} L_L} \qquad (8\text{-}6)$$

where $\overline{C^*}$ = time-weighted average vapor concentration, kg/m^3.

The results of this work are shown in Table 8-1 as "apparent" diffusivities. These results, at least in some cases, were surprisingly high. In an attempt to clarify the findings, the solubility of several of the chemicals were measured by prolonged immersion of pre-weighed pieces of the film in the liquid chemical, then, following a surface drying, the saturated film pieces were re-weighed. The weighing was done in a covered container to reduce evaporation losses during the weigh time. Diffusivities were then redetermined, using the measured solubility as the concentration driving force in equation (8-6). The results are shown as "solubility based" diffusivities in Table 8-1. The diffusivities determined by the two methods differ sharply, in some cases by more than four orders of magnitude, with the apparent diffusivity always being greater.

Thoma (1985) measured the diffusivity of these chemicals in the same film material. Thoma's methods were more sophisticated and included closer control of the temperature.

In Thoma's work, small landfill simulators were constructed of two sections of glass, 125 mm in diameter. The two sections fit together with ground-glass flanges, sealed with silicone vacuum grease. In the upper cylinder, a soil sample could be placed to be in series with the film.

A sample of the PVC film was placed above the soil, held in place by a compression ring and sealed with vacuum grease.

Table 8-1

Diffusivities of Several Chemical Vapors in a 20-mil Sample of Poly(vinylchloride) Film (Data from Surin, 1982)

Chemical	Diffusivity (at 30°C) Apparent (cm^2/s)	Solubility Based (cm^2/s)
Methanol	2.68 E-5	--
Chloroform	1.4 E-4	1.08 E-6
Dichloromethane	2.37 E-4	2.1 E-6
Bromoform	3.35 E-4	5.2 E-9
Carbon tetrachloride	1.69 E-5	7.5 E-8
Benzene	2.53 E-4	7.2 E-7
Chlorobenzene	5.03 E-4	2.4 E-7
o-Dichlorobenzene	4.96 E-4	3.4 E-8
Toluene	4.12 E-4	3.4 E-7
m-Xylene	4.73 E-4	1.9 E-7
Acetone	2.17 E-4	8.4 E-7
Diethyl Ether	1.79 E-4	--
Octane	7.05 E-5	--
Dodecane	1.06 E-3	7.2 E-8
Cyclohexane	2.18 E-5	--
n-Hexane	1.48 E-5	--
n-Pentane	2.02 E-5	--

Chemical could be added to the lower section, temperatures could be monitored in the lower section and vapor samples could be withdrawn from the lower section.

The simulator devices, when assembled, were placed in a temperature controlled room at 20±2°C. Each of the simulators were then weighed at intervals with the passage of time. Vapor samples were withdrawn by a gas-sampling syringe to determine the vapor phase composition in the lower section.

The results of Thoma's work are summarized in Table 8-2.

Several of the chemicals caused serious damage to the film after a few days exposure. In some cases the film was stretched into a bubble, and in most cases it became stiff and brittle after exposure.

The results indicate that a PVC liner will not be an effective barrier for a number of vapors. For example, if a 20-mil film were to be equivalent to about one foot of soil of 0.5 porosity, it would have an apparent diffusivity of about 3 E-5. It can be seen that this figure is exceeded for many of the chemicals examined in the case of the PVC film. Noting some of the higher apparent diffusivities in Table 8-1 leads to the conclusion that the PVC film would offer only negligible resistance in some cases.

It is commonly known that the diffusivity of organic vapors in polymers is concentration dependent, with the diffusivity increasing rapidly with increased concentration. To evaluate a polymer membrane as a landfill vapor barrier would, then require an estimate of the vapor concentration and the specific chemical diffusivity in the specific polymer film at the estimated concentration.

Based on these experimental data, it is concluded that synthetic liners may not serve adequately as vapor barriers over landfills. However, it is possible that specific films may be satisfactory barriers for specific vapors.

Table 8-2

Apparent Diffusivities of Chemical Vapors in a 20 mil Sample of Poly(vinylchloride) Film

Chemical	Diffisuvity (20°C) (cm^2/s)	Confidence Interval (90%)
Methanol	5.8 E-6	±3 E-6
Methylcyclohexane	3.3 E-6	±8 E-6
1,2 Dichloropropane	9.0 E-5	±5 E-6

9.0 LITERATURE CITED

Adamson, A. W., Physical Chemistry of Surfaces, John Wiley Inc., New York (1982), 4th Ed., p.49.

Berg, J. C., "Interfacial Phenomena in Fluid Phase Separation Process", in Recent Developments in Separation Science, Vol. II, N. Li (Ed.), CRC Press, Cleveland (1972).

Bilkaldi, F., J. D. Parsons, J. A. Mann and R. D. Newmann, J. Chem. Phys., 72, 960 (1980).

Bretton, M., et al., "Assessment of Air Emissions from Hazardous Waste Treatment, Storage and Disposal Facilities (TSDFs)- Preliminary National Emissions Estimates" - Draft Final Report -GCA Corp. for EPA-GCA Report No. GCA-TR-83-70-G (1983).

Burnett, J. C. Jr., and D. C. Himmelblau, "The Effect of Surface Active Agents on Interphase Mass Transfer", A.I.Ch.E. Journal, 16(2), 185 (1970).

Cudahy, J. J. and R. L. Standifer, "Emission Control Options for SOCMI", EPA - Research Trangle Park, North Carolina, June (1980).

Davies, J. T. and E. K. Rideal, Interfacial Phenomena, Academic Press, London, 1st Ed. (1961), p. 268.

Davies, J. T. and E. K. Rideal, Interfacial Phenomena, Academic Press, New York, 2nd Ed. (1963), Chapter 7.

Davies, J. T. and Myers, Chem. Eng. Sci., 16, 55 (1961).

Drost-Hansen,W., J. Coll. Int. Sci., 58, 251 (1977).

Drehmel, D. C., B. E. Daniel and D. Carnes, "Relative Effectiveness of Chemical Additives and Wind Screens for Fugitive Dust Control", Environmental Progress, 1,(1), 16-20 (1985).

Ehrenfeld, J. R., H. H. Ong and J. M. Bass, "Evaluation of Emission Controls for Hazardous Waste Treatment Storage and Disposal Facilities, Draft Final Report to U. S. EPA, Office of Air Quality-Planning and Standards, August (1984).

Engstrom, A., "VOC Desorption Rate Reduction by Surface Coverage with Octanol", Unpublished Report, University of Arknasas, August (1984).

Goodridge, F. and I. G. Robb, "Mechanism of Interfacial Resistance in Gas Absorption", Ind. Eng. Chem. Fundamentals, 4(1), 49-55 (1965).

Hansen, R. S., "Diffusion and the Kinetics of Adsorption of Aliphatic Acids and Alcohols at the Water-Air Interface", J. Coll. Int. Sci., 16, 549-560 (1961).

Haxo, H., et al., "Lining of Waste Impoundments and Disposal Facilities", Prepared for EPA by Metrecon Corp. SW-870 (1980).

Johnson, C. and S. Bellora, Chemical Engineering Senior Project Report, Department of Chemical Engineering; University of Arkansas, December (1984).

Kinoshita, K., H. Ishikawa and K. Shinoda, Bull. Chem. Soc. Japan, 31, 1081 (1958).

Kitagorodskii, S. A. and P. Greenberg (ed.), "The Physics of Air-Sea Interaction", Israel Program for Scientific Translation (1977).

Lunney, P. D., C. Springer and L. J. Thibodeaux, "A General Correlation for Predicting Liquid Phase Mass Transfer Coefficients in Surface Impoundments", Environmental Progress (accepted for publication).

Lunney, P. D., "Characterization of Wind and Depth Effects Upon Liquid Phase Mass Transfer Coefficients: Simulation Studies", M. S. Thesis, University of Arkansas (1983).

Levich, V. G., Physicochemical Hydrodynamics, Translated by Scripta Technica Inc., Prentice Hall, New Jersey, (1962), p. 170.

Levich, V. G., Physicochemical Hydrodynamics, Prentice Hall, New Jersey (1962)a, pages 384-394

Lewis, W. K. and G. Whitman, Ind. Eng. Chem., 16, 1215 (1924).

Lewis, J. B., Chem. Eng. Sci., 3, 248 (1954).

Millington, R. J. and J. M. Quirk, "Permeability of Porous Solids", Trans. Faraday Soc., 57, 1200-1207 (1961).

Mackay, D. and R. S. Matsugo, "Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water", Can. J. Chem. Eng., 51, Aug. (1973).

Mackay, D., Y. Cohen and W. Cocchio, "Laboratory Study of Liquid Phase Controlled Rates in Presence of Wind Waves", Env. Sci. Tech., 12, 553 (1978)

McRitchie, F. "Evaporation Retarded by Monolayers", Science, 163, 929 (1969)

McCoy, B. J., "Evaporation of Water Through Surfactant Layers", A.I.Ch.E. Journal, 28, 844-47 (1982)

Nguyen, T. N., "Investigation of Floating Immiscible Liquid as a Control Method for Volatile Organic Chemical Evaporation from Surface Impoundments", M. S. Thesis, University of Arkansas, May (1984).

Parker, R.S.P., "Fences for Reduction of Wind Enhanced Liquid Phase Mass Transfer Coefficients Over Water Bodies", M. S. Thesis, University of Arkansas, (1984).

Roulier, M., U.S. EPA, MERL, Cincinnati, February (1982) (Private Communication).

Raine, J. K. and D. C. Stevenson, "Wind Protection by Model Fences in a Simulated Atmospheric Boundary Layer", J. of Industrial Aerodynamics, 2, 159-180 (1977).

Seidell, A., Solubilities of Organic Compounds, Vol. II, Van Nostrand, New York p. 622, (1941).

Smith, J. M., D. C. Bomberger, Jr. and D. L. Haynes, "Prediction of the Volatilization Rates of High Volatility Chemicals from Natural Water Bodies", Env. Sci. Tech., 14, 1332 (1980)

Snyder, W. H., : "Similarity Criteria for the Application of Fluid Models to the Study of Air Pollution Meteorology", Boundary Layer Meteorology, 3, 113-134 (1972).

Surin, A., "Diffusion of Hazardous Chemicals Through PVC Sheets", Unpublished Report, University of Arkansas (1982).

Springer, C., K. T. Valsaraj, P. D.Lunney and L. J.Thibodeaux, "Emission of Hazardous Chemicals from Surface and Near Surface Impoundments to Air", Draft Final Report to U. S. EPA, Project No: CR-808161-02 (1985).

Springer, C. L., L. J. Thibodeaux and S. Chatrathi, "Simulation Study of the Volatilization of Polychlorinated Biphenyls from Landfill Disposal Sites", Chapter 17 in Environment and Solid Waste, Characterization, Treatment and Disposal, C. W. Francis and S. I. Auerbach (eds.), Butterworth Publishers, Woburn, MA (1983).

Springer, C., L. J. Thibodeaux, P. D. Lunney, R. S. Parker and S. C. James, "Secondary Emissions from Hazardous Waste Disposal Lagoons: Field Measurements", presented at the Ninth Annual Solid and Hazardous Waste Research Symposium, EPA, Cincinnati, March (1983).

Springer, C., L. J. Thibodeaux, and T. E. Hedden, "Thermal Effects on the Emission of Volatile Organic Chemicals from Surface Waste-Water Impoundments in the Absence of Wind: Laboratory Measurements", presented at the 77th Annual APCA Meeting, San Francisco, CA, June (1984).

Springer, C., K. T. Valsaraj and L. J. Thibodeaux, "Laboratory Investigations of In-Situ Emission Control Methods for Surface Impoundments", Paper No. 85-70.2 presented at the 78th Annual APCA Meeting, Detroit, MI, June (1985).

Sternling, C. V. and L. E. Scriven, "Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect", A.I.Ch.E. Journal, 5, 514 (1959).

Thibodeaux, L. J., D. G. Parker and H. H. Heck, "Measurement of Volatile Emissions from Wastewater Basins", Final Report prepared for U. S. EPA under Grant No. R-805534, December (1981).

Thibodeaux, L. J., Chemodynamics: Environmental Movement of Chemicals in Air, Water and Soil, John Wiley, New York (1979), Chapter 2.

Thibodeaux, L. J., "Transport of Pesticides and Related Chemicals Across Air-Water Interfaces", U. S.-USSR Symposium on Forecasting Behavior of Pesticides in the Environment- Proceedindgs, October (1981).

Thoma, G. J., "The Effectiveness of Poly(vinyl-chloride) as a Vapor Barrier for use in Hazardous Waste Landfills", M.S. Thesis, University of Arkansas, Fayetteville (1985).

Treybal, Robert E., Mass Transfer Operations, Third Ed., McGraw-Hill, New York (1980).

Valsaraj, K. T., C. Springer, T. Ngnyen and L. J. Thibodeaux, "Investigation of Floating Immiscible Liquids to Control VOC Emissions from Surface Impoundments", Proc. of the 11th Annual EPA Res. Symp., EPA-600/9-85/013, pages 145-152, April (1985).

Vogel, G. A. "Air Emission Control at Hazardous Waste Management Facilities", J. APCA, 35, 558-65 (1985).

Wetherold, R. G., B. M. Eklund and T. P. Nelson, "A Case Study of Direct Control of Emissions from a Surface Impoundment", Eleventh Annual Res. Symp. on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, U. S. EPA, April (1985)